Polar Organic Compounds in Fine Particulate Matter Sources and in the Urban Atmosphere

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Abstract

Polar organic compounds are quantified in fine particulate matter emitted from major urban air pollution sources. Fine particulate matter emissions from meat cooking, hardwood and softwood combustion, motor vehicle exhaust, and cigarette smoking, along with leaf particulate abrasion products, tire dust, brake dust, and paved road dust, are converted to trimethylsilyl derivatives and analyzed by gas chromatography/mass spectrometry. Silylation enables or improves the quantification of a number of compounds, including cholesterol and other sterols, monoglycerides, levoglucosan and related sugar anhydrides, normal alkanols, triterpenoids, and compounds derived from wood lignin, which may be suitable tracers for specific emission sources of fine particulate matter. In addition, gas phase formic and acetic acids concentrations are reported over an 8-month period at 9 sites in the Los Angeles air basin. A comparison of these concentration profiles with concentrations of other pollutants and with meteorological variables shows that both direct emissions and atmospheric chemical formation contribute to observed levels of formic and acetic acids. Finally, longer chain gas phase organic acids (from C_2 up to C_{10}) are measured during a severe photochemical smog episode in the Los Angeles area.

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1 Introduction

1.1 Motivation and Background

Airborne particulate matter is one of the most studied classes of pollutants. It is among the original set of "criteria pollutants" designated for regulation by the U.S. Environmental Protection Agency (EPA) under the mandate of the Clean Air Act of 1970 and its subsequent amendments. The federal air quality standard for particulate matter originally specified the maximum allowable mass of total suspended particles (TSP) in the air. In 1987, the national ambient air quality standard (NAAQS) for particulate matter was changed from the TSP standard to one limiting the allowable mass of particles smaller than 10 μm in diameter, PM_{10}. This change was made because medical studies indicated that particles larger than 10 μm do not penetrate as deeply into the lower respiratory tract, and therefore do not pose as serious a risk to human health (1).

There is some concern, however, that the PM_{10} standard is insufficiently stringent to safeguard public health (2, 3). Attention has focused on fine particulate matter, defined as those particles with a diameter less than about 2.5 μm ($PM_{2.5}$). Particles smaller than 2.5 μm diameter can be respired deep into the lungs and, together with gaseous pollutants such as ozone and sulfur dioxide, have been implicated as responsible for the adverse health effects associated with air pollution (4, 5). Of particular concern are the elevated concentrations of organic compounds in fine respirable particles, because many of these organics are known mutagens (6, 7) and carcinogens (8,

9). Particles with diameters from 0.1–1 μm have come under further scrutiny because particles in this size range scatter visible light most efficiently and accordingly are responsible for the deterioration in visibility observed in both polluted urban areas like Los Angeles (10) and in remote locations such as Grand Canyon National Park (11).

In 1987, the EPA established the U.S. federal primary PM_{10} standard, nominally at the level requisite to protect the public health with an adequate margin of safety, at 50 μg m^{-3} annual arithmetic mean and 150 μg m^{-3} 24-h average. The EPA promulgated new NAAQS for $PM_{2.5}$ in 1997, citing evidence of serious health effects of fine particle air pollution even at levels that met then-current standards (12). In addition to establishing a new 8-h standard for ozone and modifying the PM_{10} standard to one based on a 3-year average of the 99th percentile of 24-h average concentrations rather than the previous standard, which allowed no more than one exceedance of the PM_{10} standard per year, the 1997 NAAQS set $PM_{2.5}$ standards of 65 μg m^{-3} 24-h average and 15 μg m^{-3} annual arithmetic mean. These new standards, however, have been suspended pending a decision by the Supreme Court (13). The legal status of the NAAQS set by the EPA, however, does not affect standards set by the State of California, whose PM_{10} standards are much more stringent than those set by EPA: 50 μg m^{-3} 24-h average and 30 μg m^{-3} annual geometric mean.

Remote air far from air pollution sources typically has particulate matter concentrations of about 20 μg m^{-3} (14). Particulate matter concentrations in polluted urban areas are of course much higher. Truly hazardous levels of particulate air pollution have been reported in locations outside the United States. For example, concentrations frequently exceed 1 mg m^{-3} at sites in China (15), and in heavily polluted areas, values as high as 2 mg m^{-3} have

been reported (14).

A monitoring network established in the South Coast Air Basin (SOCAB) in the year 1986 found that at most sites within the Los Angeles metropolitan area, PM_{10} mass concentrations exceeded both the annual and 24-h average federal air quality standards (16). Los Angeles air quality has improved in recent years, particularly fine particle sulfate and elemental carbon concentrations (17), due to strict control of sulfur oxide emissions and the use of newer diesel engines and improved diesel fuels. With the exception of one day in 1995, federal 24-h PM_{10} standards were met throughout Los Angeles and Orange Counties every year from 1993–1999, the last year for which data are available (18). The federal 24-h standard was exceeded on only one monitoring day each at one location in Riverside County in 1998 and at one location in San Bernardino County in 1999. Nevertheless, the South Coast Air Basin and the San Joaquin Valley continue to be designated as federal nonattainment areas for PM_{10}, as the annual arithmetic mean standard was exceeded at several sites in Riverside and San Bernardino Counties in 1998 and 1999, and at Azusa in Los Angeles County and Anaheim in Orange County in 1998. Moreover, nearly the entire state of California–accounting for over 99% of the state's population–is exposed to PM_{10} levels that exceed state standards during at least part of the year (19, 20).

A great deal of research has been undertaken to devise optimal air pollution control strategies which will bring about the necessary reductions in ambient particulate matter concentrations at the lowest possible cost. The usual paradigm for such research has been first to identify and quantify each of the individual sources whose emissions contribute to the observed ambient air pollution problem. A mathematical model can then be constructed which simulates the important processes (e.g., dilution, transport, chemical reac-

tion, and deposition) and predicts the ambient air quality which would result if a certain prescribed emission control program were put into place. Since adopting a particular air pollution control program is a large, expensive undertaking, it is not desirable to implement emissions control strategies which are either unnecessary or insufficient to achieve the desired improvement in ambient air quality.

1.2 Research Objectives

In order to successfully model the chemistry and physics of urban air pollution with an eye toward devising effective control strategies, one of the long-term needs of the air pollution research community is to be able to measure the full range of organic compounds in the urban atmosphere, from gas phase pollutants through the semivolatiles and up to the particle phase. Polar organic compounds in atmospheric particulate matter, however, are particularly difficult to detect and quantify by gas chromatography/mass spectrometry (GC/MS) because they do not elute from the type of GC columns commonly used. Gas phase formic and acetic acids, known to be present at high concentrations during severe smog episodes, have not been studied over a large urban area over a long period, and their sources and formation mechanisms remain obscure. In addition, the atmospheric concentrations of gas phase organic acids above C_2 have seldom been studied previously. The objective of this research is to advance measurement methods to address these problems, paying special attention to particle phase organic acids and alcohols and to gas phase low molecular weight organic acids.

1.3 Approach

This thesis is divided into two parts. Polar organic compounds present in the primary emissions from the largest sources of fine organic particulate matter are examined and compared to fine atmospheric particulate matter in Chapters 2–4. Gas phase organic acids are discussed in Chapters 5 and 6. Finally, in Chapter 7 the major results are summarized and suggestions are provided for further extensions of this work.

1.3.1 Polar Particulate Matter

Hildemann et al. conducted a source sampling program to characterize the major sources of carbon particles in the Los Angeles area. The set of 13 source types studied accounted for approximately 80% of the fine organic particle emissions in the Los Angeles area in 1982 (21). Rogge et al. (22–29) quantified hundreds of individual organic compounds that are present in fine particulate matter samples from these primary fine carbon particle emissions sources and also analyzed Los Angeles area ambient aerosol samples. Individual organic compounds which were unique to a particular source type were identified for each of 10 source types. The concentrations of those tracer compounds observed in the ambient aerosol samples were then used to characterize the contributions of each source type to the fine organic aerosol in the ambient samples, with the goal of determining the relative importance of each of the individual source types to the fine aerosol burden (30).

More recently, Schauer et al. conducted a series of source sampling tests to further characterize the emissions profiles of several important sources of fine particulate matter, with special attention focused on semivolatile organic compounds that partition between the gas and particle phases (31–33). An important aspect of the source sampling programs is the use of a dilution

stack sampling device (34), in which hot source emissions are diluted with purified air, allowing supersaturated organic compounds time to cool to ambient temperatures and condense onto existing particles present in the source effluent within the sampling system.

One difficulty encountered by Rogge et al. was that many of the organic compounds present in fine particulate matter are too polar to elute from the standard types of GC columns typically used for particulate air pollution analysis. In order to quantify the concentrations of some of the fine particle carboxylic acids, Rogge et al. reacted an aliquot of each source and ambient sample extract with diazomethane (CH_2N_2). Many of the organic acids are methylated in this procedure, forming fatty acid methyl esters which are nonpolar and therefore more readily elutable under the chromatographic conditions used in their study:

$$RCOOH \xrightarrow{CH_2N_2} RCOOCH_3$$

Many of the organic compounds present in some of the source sample effluents, as well as in atmospheric samples, are not effectively mobilized by this procedure.

The objective of the first portion of the present research program is to further advance methods for the detection and quantification of highly polar organic compounds in source emissions and in airborne particulate matter samples. To render the compounds of interest less polar and thus chromatographable, they are treated with a strong silylating reagent, bis(trimethylsilyl)trifluoroacetamide (BSTFA), to convert them to trimethylsilyl (TMS) ester and ether derivatives:

$$RCOOH \xrightarrow{BSTFA} RCOOSi(CH_3)_3 \quad \text{(ester)}$$

$$ROH \xrightarrow{BSTFA} ROSi(CH_3)_3 \quad \text{(ether)}$$

The trimethylsilyl group on each of the derivatized compounds yields a distinctive mass fragmentation pattern which is easy to detect. Furthermore, by improving the chromatographability of the polar compounds, silylation enhances response factors, and thus gives lower detection limits. Silylated extracts of oceanic dust fallout (35) and rural aerosols (36) have been examined to identify alcohols separately from wax alkanes and acids. Urban air pollution studies, however, have yet to benefit from such techniques. Compounds such as cholesterol, which has been developed as an urban meat smoke tracer but which is very hard to measure at the low ambient concentrations of atmospheric samples (22, 30), is much more readily detected following silylation. Extensive work, however, is needed to develop such methods for use on urban air pollutant particle samples because not all silyl esters and ethers of interest are presently in the National Institute of Standards and Technology (NIST) mass spectral library.

Tentative identification of those polar organic compounds that react to form TMS derivatives is accomplished through comparison against the NIST mass spectral library where possible and by fundamental interpretation of the mass spectra. Compounds tentatively identified in this manner are confirmed, to the extent possible, by silylation of authentic standards of those compounds and recording of their mass spectra. In this manner, a library of the mass spectra of silyl esters and ethers relevant to the analysis of atmospheric aerosol samples and source samples has been created. Through this process, new tracer compounds for particular source types are discovered. Environmental models that are used for planning air pollution source abatement strategies then can be modified in light of these new findings.

1.3.2 Gas Phase Organic Acids

Gas phase organic acids are a class of low molecular weight compounds about which relatively little is understood. In particular, numerous studies have shown that formic and acetic acids are major trace constituents of both remote and polluted air (37, 38). Several possible emissions sources and gas phase production routes have been hypothesized, but modeling studies incorporating these mechanisms have generally failed to account satisfactorily for the high concentrations frequently observed (39–41). Chapter 5 reports the atmospheric concentrations of formic and acetic acids at nine sites in the Los Angeles area over an eight-month period in 1986. The seasonal and spatial variations in the atmospheric concentrations of formic and acetic acids are analyzed to assess the relative importance of primary emissions vs. secondary formation in the atmosphere by gas phase or aqueous phase chemical reaction to the observed ambient concentrations.

In 1993, a 48-h intensive urban air sampling program was conducted at four sites in the Los Angeles basin (42). The experiment was designed to characterize the full range of gas phase, semivolatile, and particle phase organic species. As part of that experiment, gas phase acids were collected on quartz fiber filters that had been pretreated with potassium hydroxide. Typically, gas phase organic acids are analyzed using ion chromatography (IC). Formic and acetic acids are generally present in sufficient concentrations to be detected readily by this technique. However, the sensitivity is insufficient to detect organic acids $> C_2$ by IC. GC/MS is much more sensitive and accordingly has the potential to be used to detect a much larger range of gas phase organic acids. These compounds are too polar, however, to elute from most GC columns without first undergoing derivatization. Chapter 6 describes the GC/MS analysis of atmospheric C_2–C_{10} organic acids concen-

trations during a severe photochemical smog episode in Los Angeles using the derivatization technique of Kawamura et al. (43).

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2 Highly Polar Organic Compounds Present in Meat Smoke

2.1 Introduction

Meat cooking operations are a major source of organic particulate matter emissions to the urban atmosphere. Meat frying and charbroiling together account for approximately 20% of all fine ($d_p < 2$ μm) organic aerosol released into the atmosphere within an 80 $\times$ 80 km area surrounding Los Angeles (1). Comparative analysis of meat smoke aerosol and urban ambient particulate matter shows that certain fatty acids (e.g., palmitic acid, stearic acid, and oleic acid) as well as cholesterol could be used as possible markers for the presence of meat smoke in the urban atmosphere (2). Receptor modeling analysis based on the use of such organic molecular tracers shows that meat smoke on average accounts for approximately 7% of the airborne fine particle mass concentration in Los Angeles area ambient air (3). The application of organic molecular tracer analysis for determination of meat smoke concentrations in the urban atmosphere, however, is impeded by the difficulty in detecting cholesterol at low concentrations in an atmospheric sample. Fatty acids such as *n*-octadecanoic acid (stearic acid) are emitted from so many sources in addition to meat smoke (see Figure 3 in reference 3) that data on their concentration alone is insufficient to determine the quan-

Reference: Nolte, C. G.; Schauer, J. J.; Cass, G. R.; Simoneit, B. R. T. Highly Polar Organic Compounds Present in Meat Smoke. *Environ. Sci. Technol.*, **1999**, 3313–3316.

tity of meat smoke aerosol in ambient air. Further, only 10% of the fine particulate organic compound mass present in meat cooking source samples has been assigned to specific compounds to date (2, 4). These factors indicate that additional tracer compounds for meat smoke aerosol should be sought through advances in analytical methods.

One way to extend the analysis of organic compounds present in meat smoke is through the formation of trimethylsilyl (TMS) derivatives, which are generally more volatile than their parent molecules. Some polar organic compounds which will not elute from a gas chromatographic column in their underivatized form, such as monoglycerides, are more readily detected following their silylation. Other compounds which are difficult to detect in their underivatized form, such as cholesterol, have greatly improved detection limits following silylation. The purpose of this paper is to develop a method for the enhanced characterization of polar compounds in meat smoke as TMS derivatives and to report the detection in the ambient atmosphere of these same compounds derived from meat smoke.

2.2 Experimental Methods

2.2.1 Sample Collection

A detailed discussion of the meat smoke source sampling protocol used to collect the samples examined has been described previously (4); only a brief description will be presented here. One hundred twelve quarter-pound (113 g) hamburger patties with a 20% fat content were charbroiled for approximately 5 minutes each until they were medium-well done (4). The resulting smoke was drawn through an overhead exhaust hood and was introduced to the source sampling system, located on the roof of the kitchen. The source sampling system used was a dilution sampler, which simulates processes that

occur under ambient conditions in the plume downwind of a source by allowing organic vapors present in the hot exhaust to cool via dilution with purified air followed by condensation of those organic vapors that will form aerosol onto existing particles within the sampler. Large particles were removed by AIHL cyclone separators operated with a 50% cutoff aerodynamic diameter of 2 μm. Fine aerosol samples were collected on Teflon membrane filters (Gelman Teflo, 2.0 μm pore size) and also on quartz fiber filters (Pallflex 2500 QAO), which had been prebaked at 550 °C for at least 12 h to reduce organic contamination. Gravimetric analysis of the samples collected on Teflon filters showed that the fine particle mass emission factor was 19 g of fine particulate matter per kg of meat cooked.

During the 1995 Integrated Monitoring Study (IMS95), 24-h average atmospheric fine particulate matter samples were collected daily at three sites in the San Joaquin Valley of California over the period from December 5, 1995, to January 6, 1996 (5, 6). The atmospheric samples analyzed here were collected over the period January 4–6, 1996, at Bakersfield, CA, and were composited, extracted, and analyzed as described below in the same manner as the meat smoke source samples.

2.2.2 Sample Extraction and Analysis

The quartz fiber filter extraction protocol used here is described in greater detail elsewhere (2, 4, 7). Prior to extraction, filters from each experiment were spiked with perdeuterated tetracosane (n-$C_{24}D_{50}$) as a recovery standard. The samples were then extracted with hexane (twice successively) and with benzene/isopropanol (2:1 mixture; three successive extractions) by mild ultrasonic agitation at room temperature. The extracts were filtered, combined, and reduced to a volume of approximately 250 μL.

One aliquot of each extract was previously derivatized by addition of diazomethane (4, 6). This enabled the detection of large quantities of free fatty acids, particularly palmitic acid, stearic acid, and oleic acid, as their corresponding methyl esters (4). In the present work, a silylating reagent (Pierce Chemical Company, Rockford, IL) consisting of bis(trimethylsilyl)trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) as a catalyst was used to derivatize a separate aliquot of each neutral (unmethylated) sample extract. Samples were spiked with 1,2,4-butanetriol as an internal silylation standard to verify that the derivatization was quantitative. Upon addition of the silylating reagent the samples were sealed and placed in an oven at 70 °C for three hours. Within several hours after derivatization, samples were analyzed by gas chromatography/mass spectrometry (GC/MS) on a Hewlett-Packard GC/MSD (GC Model 6890; MSD model 5973) using a 30-m DB-5 column (0.25 μm film thickness, 0.25 mm ID; J&W Scientific). The oven temperature programming was as follows: (1) isothermal hold at 65 °C for 10 min, (2) temperature ramp at 10 °C min^{-1} to 310 °C, and (3) isothermal hold at 310 °C for another 25 min.

Only compounds that are in addition to those previously reported for these source samples by Schauer et al. (4) are discussed here, along with cholesterol which is of particular interest due to the present ability to detect and quantify this compound more accurately as its TMS derivative. Initial compound identification was made by matches to standard reference spectra in the National Institute of Standards and Technology (NIST) mass spectral library. The identifications for each compound were confirmed by comparison with authentic standards. The mass of individual organic compounds collected on the filters was determined by replicate analysis according to the recovery of the internal standard n-$C_{24}D_{50}$, with an average precision of

approximately ± 20%.

2.3 Results and Discussion

The fat in uncooked meat occurs as triglycerides, which consist of three fatty acids esterified to a glycerol backbone. During the cooking process, triglycerides can be hydrolyzed or thermally oxidized (8), yielding free glycerol, mono- and diglycerides, and free fatty acids, as shown schematically in Figure 2.1. Free fatty acid emission factors for this meat smoke sample have been reported previously (4). A total ion chromatogram showing the compounds detected in the silylated charbroiled meat smoke extract, including several monoglycerides and cholesterol, is shown in Figure refmeatchromatfiga. Calculated compound emission factors are presented in Table 2.1 and the chemical structures of the compounds measured are given in Figure 2.3. The C_{16} monoglycerides, 1-palmitin and 2-palmitin, are by far the most abundant, and there are significant emissions of C_{18} (1-stearin) and $C_{18:1}$ (1-olein) monoglycerides as well. The total class emission factor for the monoglycerides in the meat smoke is approximately 20% of the analogous emission factor reported for the summation of the alkanoic plus alkenoic acids (4).

In addition to the free fatty acids, monoglycerides, and glycerol mentioned above, the breakdown of triglycerides also yields the minor products shown in Figure 2.1. Trace levels of ethylene glycol, propane-1,2-diol, and 1-hexadecanoylethanediol were detected in the meat smoke sample. These compounds were not quantified, however, due to their low concentrations.

2.3.1 Detection of Meat Smoke Tracers in the Atmosphere

Data from previous source tests show that fatty acids, particularly stearic acid and palmitic acid, are emitted from a variety of source types including

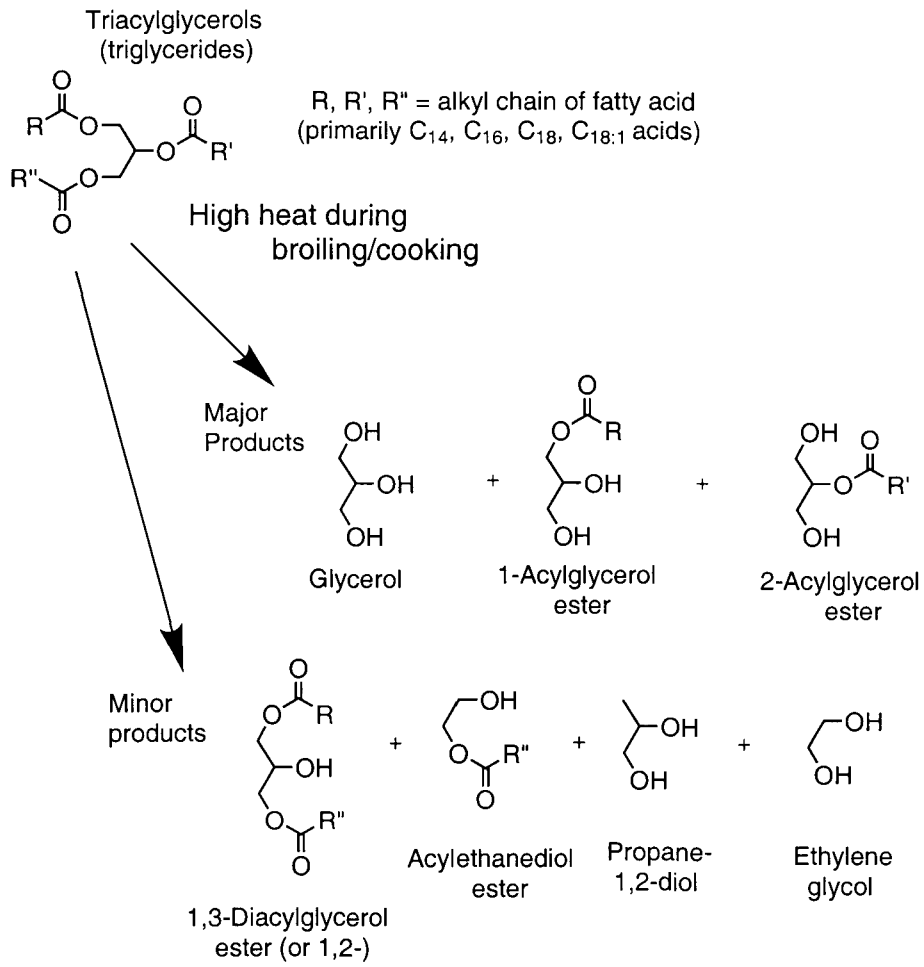

Figure 2.1: Diagram showing breakdown products of triglycerides.

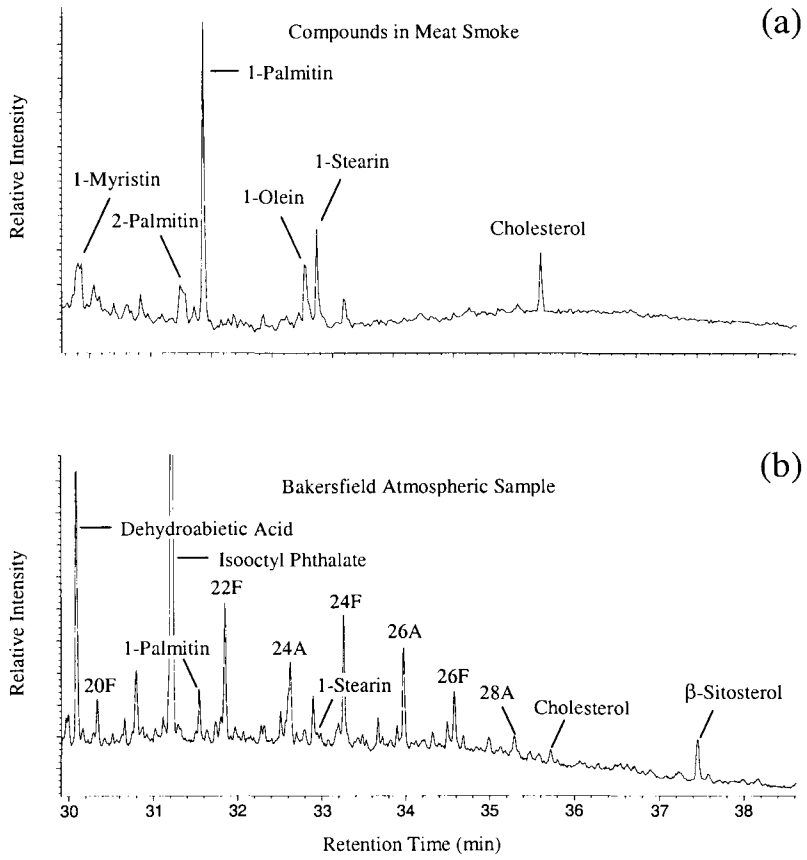

Figure 2.2: Total ion GC/MS chromatogram of fine particle polar organic compounds detected in (a) charbroiled hamburger meat smoke and (b) atmospheric sample collected in Bakersfield, CA, January 4–6, 1996. The compounds shown were detected as trimethylsilyl derivatives. Compounds labelled A and F denote straight-chain alcohols and fatty acids, respectively. Other compound structures are given in Figure 2.3.

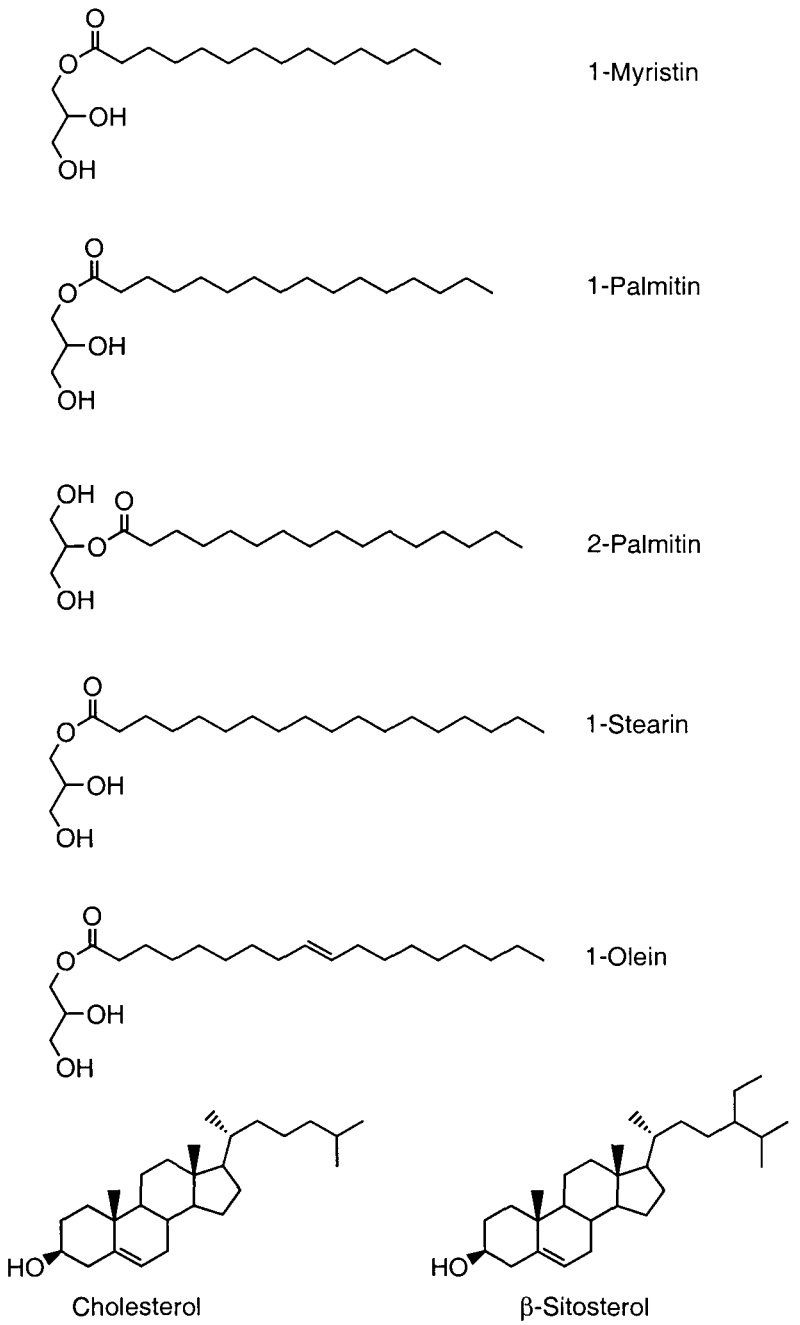

Figure 2.3: Structures of compounds detected in meat smoke and in atmospheric fine particulate matter collected January 4–6, 1996, in Bakersfield, CA.

Table 2.1: Polar organic compounds detected in charbroiled meat smoke and in the atmosphere.

Compound	Emission Factor[a]	Atmospheric Concentration[b]
1-myristin (C_{14})	6.	0.4
1-palmitin (C_{16})	50.	7.3
2-palmitin (C_{16})	10.	1.4
1-stearin (C_{18})	21.	3.1
1-olein ($C_{18:1}$)	15.	nd[c]
glycerol	12.	28.
cholesterol	29.	5.0

[a] μg per g of meat cooked.
[b] Detected in sample collected January 4–6, 1996, in Bakersfield, CA (ng m^{-3}).
[c] not detected

meat cooking (2, 6), motor vehicle exhaust (9, 10), road and tire dust (11), cigarette smoke (12), roofing asphalt (13), and fuel oil combustion (14). For this reason we do not recommend that fatty acids alone be considered as primary tracers for meat smoke aerosol. Instead an assemblage of compounds viewed as a group is more useful as an indicator of the quantity of meat smoke in the atmosphere. Of this combination of tracer compounds, cholesterol appears to be most useful (2), supplemented by monoglycerides and possibly oleic acid and nonanal in the correct proportions (3).

The levels of cholesterol in ambient air fine particulate matter samples are often too low to be detected reliably by previous analytical methods (2, 3). Following silylation, however, cholesterol is easily detected in the San Joaquin Valley atmospheric samples, and some of the monoglycerides identified in the meat smoke are found as well. The total ion GC/MS chromatogram of the silylated Bakersfield January sample is shown in Figure 2.2b. Compound atmospheric concentrations are listed in Table 2.1, and their distributions

Table 2.2: Distribution of polar organic compounds in charbroiled meat smoke and in the atmosphere relative to 1-palmitin.

Compound	Meat Smoke	Atmosphere[a]
1-myristin (C_{14})	0.12	0.05
1-palmitin (C_{16})	1.	1.
2-palmitin (C_{16})	0.20	0.19
1-stearin (C_{18})	0.42	0.42
1-olein ($C_{18:1}$)	0.30	nd[b]
glycerol	0.24	3.8
cholesterol	0.58	0.68

[a]Detected in sample collected during January 4–6, 1996, in Bakersfield, CA.
[b]not detected

relative to 1-palmitin are presented in Table 2.2.

The compounds cited above are not viewed as unique tracers for meat smoke, but rather a mass balance on all sources of each compound must be satisfied in order to quantify meat smoke concentrations in the atmosphere as illustrated by Schauer et al. (3). In this context, other sources of cholesterol must be considered, including small amounts found in cigarette smoke (12). In a particular location there could be specialized industrial applications, such as soap manufacturing, that process meat fats and if present those emissions would have to be included in the mass balance calculations as well. That such mass balance calculations are likely to succeed can be seen from the data in Table 2.2. The distribution of the saturated monoglycerides (myristin, 1- and 2-palmitin, and stearin) and cholesterol shows substantial agreement between the meat smoke source sample and the representative atmospheric sample. The C_{18} unsaturated monoglyceride 1-olein was not found in any atmospheric sample despite its relatively high concentration in the meat smoke. This suggests that 1-olein has a short atmospheric

lifetime, possibly due to reaction of ambient ozone with this unsaturated organic compound. By contrast, glycerol was found to be highly enriched in the atmospheric samples relative to its concentration in the meat smoke source samples, suggesting that there may be other important emissions sources for that compound.

In future work, the effluents from other major fine particle sources will be examined by silylation to quantify polar organic compounds which can be used in chemical mass balance receptor modeling calculations like those of Schauer et al. (3).

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3 Highly Polar Organic Compounds Present in Wood Smoke and in the Ambient Atmosphere

3.1 Introduction

Airborne particulate matter is of concern primarily because of its impact on human health (1) and also because it leads to decreased visual range both in urban areas (2) and remote areas (3), including national parks (4, 5). One important source of fine particles in urban areas during the winter months is the combustion of wood in residential stoves and fireplaces, which contributes an estimated 10–30% of the atmospheric fine particulate matter burden (6–10). Extracts of wood smoke particles have been shown to be mutagenic (11–14), and wood smoke particles are predominantly in the inhalable size range (6, 7, 11, 13), thus increasing their importance as a factor that can affect human health.

Organic chemical tracer-based studies of the relative contribution of wood smoke, vehicle exhaust, meat cooking smoke, road dust, and other sources of atmospheric fine particulate matter (9) would benefit from the identification of additional compounds which can be used as specific tracers for wood smoke. Gas phase combustion byproducts such as NO_x, HCN, CH_3CN, CH_4, and CH_3Cl have been used to assess the contribution of emissions from biomass burning to ambient levels of particulate matter (15), but none of

these gaseous species are unique to biomass combustion, and furthermore CH_3Cl is widely used in industry. Other investigators have used non-mineral potassium as a tracer for wood smoke, but there exist other sources of potassium such as meat cooking and refuse incineration (16, 17). Highly variable concentrations of potassium in wood smoke particles (18) and in soil particles further detract from its suitability as a tracer for wood smoke. Other investigators have focused on polycyclic aromatic hydrocarbons (PAH) as potential wood smoke tracers (19, 20), but these are not unique to wood combustion. PAH emissions during wood combustion are highly sensitive to burn rate (21), and some PAH are transformed rapidly by atmospheric chemical processes such that PAH ratios in the atmosphere will depart from those seen in source emissions (9). Retene has been proposed as a specific tracer for wood smoke (22), but it is only present in the smoke from coniferous woods (gymnosperms) and is a semivolatile organic compound with a relatively high vapor pressure, making its quantification more difficult. Other studies have used ^{14}C as a tracer for contemporary carbon since it is depleted in fossil fuels (6, 8, 23), but there are numerous sources of contemporary carbon in addition to wood combustion (24), and the technique is relatively expensive.

Levoglucosan, formed during the pyrolysis of cellulose, is emitted in large quantities during wood combustion (21, 25, 26) and, to a lesser extent, cigarette combustion (27). It has been shown to be stable under simulated atmospheric conditions (28) and has been detected in remote locations far from combustion sources, including sites in the Atlantic Ocean (29). Since levoglucosan has no known non-combustion sources, it is potentially a very useful tracer for wood smoke in the atmosphere.

Phenolic compounds from the thermal breakdown of lignin have also been proposed as potentially useful tracers for wood smoke, since many of them

are emitted in relatively high quantities and are specific to wood combustion sources (30–34). Elias et al. have reported using high-temperature gas chromatography to detect large polar molecules with very high melting points that are present in biomass smoke (35).

The purpose of this paper is to report the use of silylation of wood smoke extracts followed by GC/MS analysis as a means for quantifying some of the most polar organic compounds present in the smoke. As a result *n*-alkanols, plant sterols, some sugars, and other compounds not previously measured in wood smoke particles can be quantified for the first time. Wood smoke tracers detected in smoke extracts will also be sought in ambient air samples collected in California's San Joaquin Valley.

3.2 Experimental Methods

3.2.1 Sample Collection

Three types of wood (pine, oak, and eucalyptus) were burned in the wood combustion tests. Only one specific type of wood was burned in each test, other than a few sheets of newspaper used to ignite the kindling. The mass of the wood burned during each test was determined as the difference in the mass of the wood prior to the test and the mass of the ashes remaining at the end; the ashes never amounted to more than a few percent of the original wood mass.

The wood combustion source tests were conducted in a residential fireplace. Emissions were withdrawn from a port in the chimney approximately 5 m above the fireplace grate. The source sampling system used was a dilution sampler, which simulates processes that occur under ambient conditions in the plume downwind of a source by allowing organic vapors present in the hot exhaust to cool via dilution with purified air followed by condensation of

those organic vapors that will form aerosol onto existing particles within the sampler. Large particles were removed by AIHL cyclone separators operated with a 50% cutoff aerodynamic diameter of 2 μm. Fine aerosol samples were collected on Teflon membrane filters (Gelman Teflo, 2.0 μm pore size) and also on quartz fiber filters (Pallflex 2500 QAO), which had been prebaked at 550 °C for at least 12 h to reduce organic contamination. Further details of the wood smoke source sampling procedure are described by Schauer (27) and by Schauer et al. (36).

Atmospheric fine particulate matter samples were collected daily at three sites in the San Joaquin Valley of California over 24-h periods (from noon to noon) from December 5, 1995 to January 6, 1996, as part of the state of California's IMS95 air quality study (37, 38). The atmospheric samples analyzed here were collected at the Kern Wildlife Refuge (KWR) and at urban sites in Bakersfield and Fresno, CA. Fine particle samples ($d_p < 3$ μm) were collected on 102 mm diameter prebaked quartz fiber filters (Pallflex Tissuequarts 2500 QAO) using a high volume dichotomous sampler (39) operating at a flowrate of 175 L min^{-1}. At each location, composites were formed from portions of both samples taken over the two consecutive 24-h periods from January 4–6, 1996. For the Fresno and Bakersfield samples, two fifths of each filter were used in making the composite, while for the KWR sample, one half of each filter was used. These composite samples, with an equivalent air volume of 200–250 m^3, were extracted and analyzed as described below in the same manner as the wood smoke source samples.

3.2.2 Sample Extraction and Analysis

The quartz fiber filter extraction protocol used here is described in greater detail elsewhere (27, 38, 40, 41). Prior to extraction, filters from each exper-

iment were spiked with a mixture of deuterated internal recovery standards, including hexanoic acid-D_{11}, decanoic acid-D_{19}, pentadecane (n-$C_{15}D_{32}$), and tetracosane (n-$C_{24}D_{50}$). The samples were then extracted with hexane (twice successively) and with benzene/isopropanol (2:1 mixture; three successive extractions) by mild ultrasonic agitation at room temperature for 10 min each extraction. The extracts were filtered, combined, and reduced to a volume of approximately 250 μL.

In the present work, a silylating reagent (Pierce Chemical Company, Rockford, IL) consisting of bis(trimethylsilyl)trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) as a catalyst was used to derivatize a 5–10 μL aliquot of each sample extract, converting hydroxyl and carboxylic acid groups to trimethylsilyl (TMS) ethers and TMS esters, respectively. Samples were spiked with 1,2,4-butanetriol as an internal silylation standard to verify that the derivatization was driven to completion. Upon addition of the silylating reagent (ca. 20 μL) the samples were sealed and placed in an oven at 70 °C for 2 h. Within several hours after derivatization, samples were analyzed by gas chromatography/mass spectrometry (GC/MS) on a Hewlett-Packard GC/MSD (GC Model 6890; MSD model 5973) using a 30-m HP-5MS column (0.25 μm film thickness, 0.25 mm ID). The oven temperature programming was as follows: (1) isothermal hold at 65 °C for 10 min, (2) temperature ramp at 10 °C min^{-1} to 310 °C, and (3) isothermal hold at 310 °C for another 25 min.

Only compounds that undergo silylation are reported here, with attention focused on those compounds not previously reported for these source samples by Schauer et al. (36). Initial compound identification was made by matches to standard reference spectra in the Wiley and National Institute of Standards and Technology (NIST) mass spectral libraries. The compound iden-

tifications were confirmed by comparison with authentic standards, where available. In the data tables that follow, clear distinction is drawn between those compounds positively identified and quantified via comparison to authentic standards versus those compounds tentatively identified via library matches and fundamental interpretation of the mass spectra. The mass of individual organic compounds collected on the filters was determined by replicate analysis according to the recovery of the internal standards deuterated hexanoic acid and n-$C_{24}D_{50}$, with an average precision of approximately $\pm$ 20%. For those compounds for which no authentic standard was available, response factors were estimated from those for analogous compounds.

3.3 Results and Discussion

Natural wood is a complex and highly variable material consisting of two major chemical components, carbohydrates and lignin. Cellulose, the basic structural material constituting 40–45% of the mass of dry wood, is a long-chain, linear polysaccharide composed of glucose monomers (see Figure 3.1). Other lower molecular weight polysaccharides, known as hemicelluloses, are bound to the cellulose skeleton as a matrix substance and make up 25–35% of dry wood mass (42, 43). During wood combustion, the cellulosic materials decompose and yield various breakdown products, including levoglucosan and the related anhydro sugars shown in Figure 3.1 (26, 44). Calculated polar organic compound emission factors from the wood combustion experiments are presented in Table 3.1. Emission factors are expressed in micrograms per gram of wood burned in the experiment. Ambient concentrations in nanograms per cubic meter for the atmospheric samples are also presented in Table 3.1.

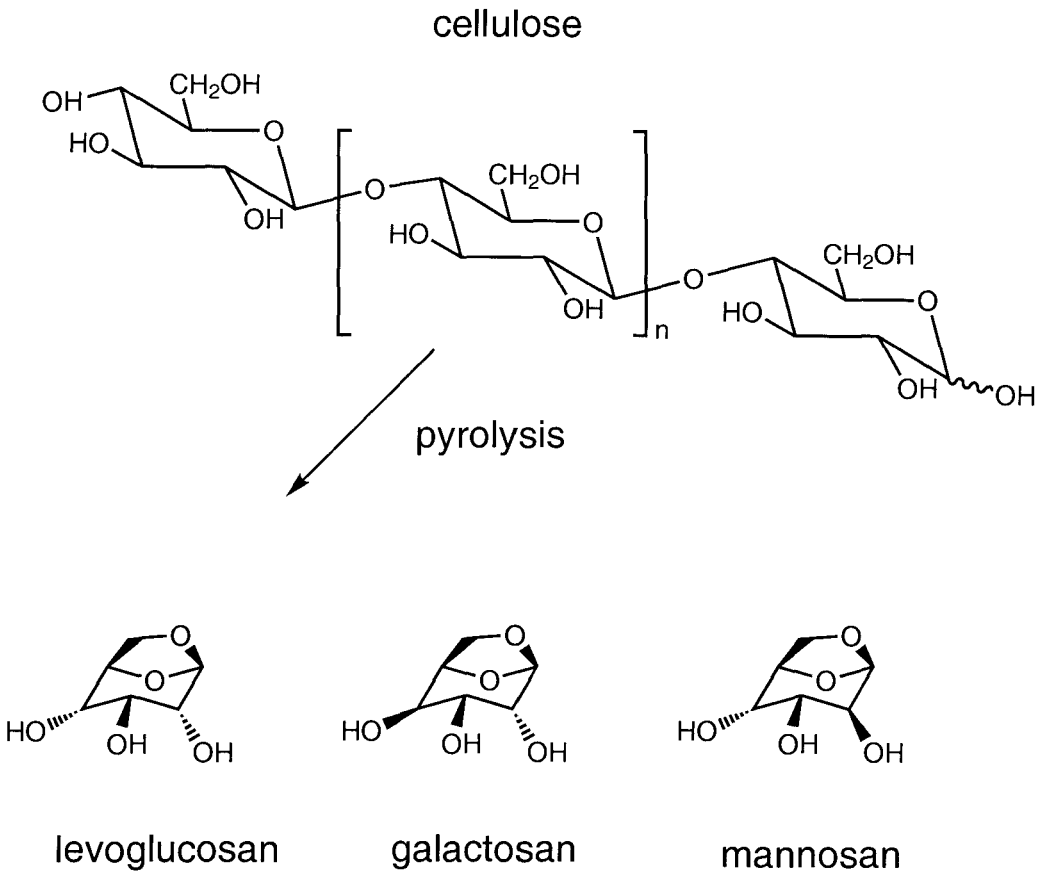

Figure 3.1: Pyrolysis of cellulose to form the sugar anhydride levoglucosan. Galactosan and mannosan are similarly derived from hemicelluloses.

3.3.1 Sugars

The most abundant compound found in all wood smoke samples and in all ambient atmospheric fine particulate matter samples is levoglucosan. Levoglucosan is present in the urban atmospheric samples at very high concentrations, exceeding 2 μg m^{-3} at Bakersfield and nearly reaching 3 μg m^{-3} at Fresno, making it a candidate for the most abundant single particle phase organic compound in the atmosphere. For this reason and because of its universal appearance in all wood smokes, levoglucosan has been proposed previously as an important tracer for use in tracking wood smoke in the atmosphere (21, 26). In this study we identify the analogous compounds galactosan and mannosan as present at high concentrations along with levoglucosan. Levoglucosan, galactosan, and mannosan are sugar anhydrides formed during combustion of cellulose and hemicellulose, as depicted in Figure 3.1. Other sugars detected via silylation include the monosaccharides xylose, mannose, and glucose. Relative to their concentrations in the wood smoke samples examined here, these monosaccharides are proportionally much more abundant in the ambient samples, particularly at the urban sites, than levoglucosan, implying that there exists an additional source for these monosaccharides in the atmosphere besides primary emissions from the woods burned here. Maltose, a disaccharide consisting of two glucose monomers, and sucrose, a disaccharide of glucose and fructose, are also found in the wood smoke and in the atmospheric samples.

Each of the compound identifications in this compound class was confirmed by comparison to an authentic standard, with the exception of glucose, which was identified on the basis of a match with the Wiley and NIST mass spectral libraries. In addition, 10 compounds with spectra similar to the other sugars were found which did not match any of the compounds in

Table 3.1: Sugars detected in wood smoke and in the atmosphere of the San Joaquin Valley, California.

Compound	Emission Factor[a]			Concentration (ng m^{-3})			
	Oak	Eucalyptus	Pine	KWR[b]	Bakersfield	Fresno	Code[c]
Anhydrides							
galactosan	30.	24.	108.	4.1	96.	144.	a
mannosan	39.	42.	340.	7.0	171.	322.	a
levoglucosan	673.	1490.	1380.	106.	2390.	2980.	a
Monosaccharides							
xylose	0.1	1.1	nd[d]	0.7	9.1	17.	a
mannose	0.2	0.7	1.5	4.5	9.3	13.	a
glucose	0.5	0.8	0.7	5.4	10.	15.	b
Disaccharides							
sucrose	0.3	0.2	0.2	0.9	4.0	3.2	a
maltose	2.8	5.0	11.	nd	3.2	4.0	a
other sugars[e]	84.	150.	80.	15.	114.	146.	c

[a] μg per g of wood burned.

[b] Kern Wildlife Refuge, San Joaquin Valley, CA.

[c] Compound identification code: a, authentic standard; b, library match, quantification based on comparison to analogous compound; c, compound class tentatively identified from mass spectrum.

[d] Not detected.

[e] Sum of 10 unknown sugars.

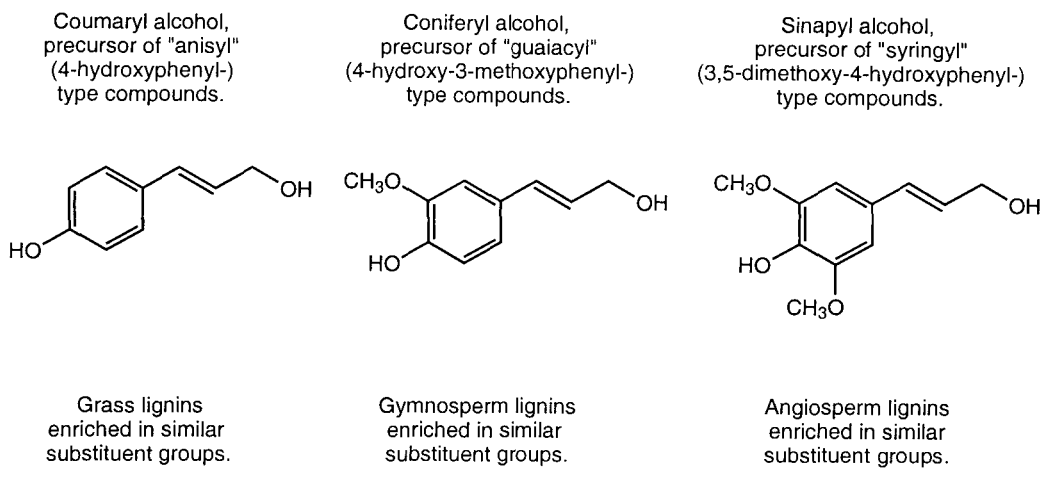

Figure 3.2: Primary building blocks of lignin (34, 43). These moieties are present in the lignin pyrolysis products listed in Table 3.2.

the mass spectral library. Their response factors were estimated by comparison to other sugars, and their concentrations are summed and reported as "other sugars" in Table 3.1.

3.3.2 Lignin Breakdown Products

Lignin, constituting 18–35% of wood by mass, is an irregular polymer of variously bonded hydroxy- and methoxy-substituted phenylpropane units (42, 43). The precursors of lignin biosynthesis are *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (see Figure 3.2). Coumaryl alcohol is the predominant lignin unit in grasses but is not prevalent in softwoods or hardwoods. Coniferyl alcohol is the predominant precursor in softwoods (gymnosperms), while both coniferyl and sinapyl alcohol-derived units are present in hardwoods (angiosperms). Pyrolysis of wood lignin yields carbonyl, alcohol, and acid breakdown products, generally with the retention of the original substituents (OH, OCH_3) on the phenyl ring in the guaiacyl and syringyl moieties

(34). The relative distribution of guaiacyl and syringyl functional groups (derived from coniferyl alcohol and sinapyl alcohol, respectively) in atmospheric particulate matter samples can yield information on the types of plant material from which they originate.

Wood smoke emission factors and atmospheric concentrations of 34 lignin decomposition products are presented in Table 3.2. Lignin nomenclature has not been standardized, and there are several different naming systems commonly used for many compounds. Accordingly, chemical structures are provided in Figures 3.3–3.5 for each compound listed in Tables 3.2 and 3.3. The lignin pyrolysis products are major compounds in the wood smoke fine particulate matter, and are also detected in the urban atmospheric samples. The first group of phenolic lignin compounds (I–XIII) in Table 3.2 consisting of carbonyl and alkyl derivatives of guaiacol and syringol have been identified previously in underivatized form in these same samples (27, 36). Silylation enables the detection of a large number of additional lignin pyrolysis products, including guaiacyl and syringyl alcohols and acids. These compounds, many of which have not been quantified previously in wood smoke samples, are grouped separately in Table 3.2.

As can be seen in the data in Table 3.2, the pine wood smoke contains large quantities of lignin products derived from coniferyl alcohol, e.g., vanillin (I), acetovanillone (III), guaiacyl acetone (VI), coniferyl aldehyde (VIII), guaiacylpropanol (XVIII), *trans*-coniferyl alcohol (XXII), and vanillic acid (XXVI), while compounds derived from sinapyl alcohol, e.g., syringaldehyde (II), acetosyringone (IV), and syringyl acetone (VII), are generally not detected. By contrast, in the case of oak and eucalyptus, the two hardwoods studied, syringyl compounds derived from sinapyl alcohol are generally more abundant in the wood smokes than their guaiacyl analogs derived

Table 3.2: Lignin breakdown products detected in wood smoke and in the atmosphere of the San Joaquin Valley, California.

Structure Number[b]	Compound	Emission Factor (μg g^{-1})[a] Oak	Eucalyptus	Pine	Concentration (ng m^{-3}) KWR[c]	Bakersfield	Fresno	Code[d]
	Carbonyl and Alkyl Products							
I	vanillin	3.2	3.4	15.	0.5	4.8	6.3	a
II	syringaldehyde	35.	41.	nd[e]	0.1	23.	14.	a
III	acetovanillone	5.3	6.4	32.	nd	4.0	4.5	a
IV	acetosyringone	17.	31.	0.1	0.2	18.	13.	a
V	propionylsyringol	2.6	3.9	nd	nd	2.6	1.8	b
VI	guaiacyl acetone	12.	14.	41.	0.3	0.5	0.6	b
VII	syringyl acetone	68.	106.	nd	nd	3.7	1.6	b
VIII	coniferyl aldehyde	22.	11.	125.	nd	0.8	nd	b
IX	sinapyl aldehyde	16.	18.	nd	nd	nd	nd	b
X	isoeugenol	1.0	0.5	17.	nd	nd	nd	a
XI	allylsyringol	17.	2.5	nd	nd	nd	nd	b
XII	*cis*-syringylprop-1-ene	14.	0.3	nd	nd	nd	nd	b
XIII	*trans*-syringylprop-1-ene	52.	0.8	nd	nd	1.6	1.1	b
	Alcohols							
XIV	4-hydroxyphenylethanol	35.	3.5	0.5	0.2	2.1	1.4	a
XV	homovanillyl alcohol	0.8	0.6	2.3	0.2	0.2	0.2	a
XVI	homosyringyl alcohol	0.9	0.9	0.1	nd	0.1	nd	b
XVII	4-hydroxyphenylpropanol	0.4	0.2	1.8	0.1	nd	nd	b
XVIII	3-guaiacylpropanol	9.7	6.5	24.	0.1	2.3	2.4	b
XIX	3-syringylpropanol	4.5	1.6	nd	nd	0.1	nd	b
XX	*para*-coumaryl alcohol	0.5	0.1	1.6	nd	nd	nd	a
XXI	*cis*-coniferyl alcohol	1.3	1.0	3.0	nd	0.1	nd	b
XXII	*trans*-coniferyl alcohol	6.6	3.6	18.	nd	0.3	0.5	b
XXIII	*cis*-sinapyl alcohol	3.1	0.9	nd	nd	0.2	nd	b
XXIV	*trans*-sinapyl alcohol	2.8	0.1	nd	nd	0.1	nd	b
	Acids							
XXV	4-hydroxybenzoic acid	1.2	2.4	2.5	0.6	7.8	12.	b
XXVI	vanillic acid	3.5	6.8	8.5	0.3	7.4	11.	a
XXVII	syringic acid	5.7	22.	nd	0.2	12.	13.	a
XXVIII	homovanillic acid	0.6	2.3	1.7	nd	1.6	2.8	a
XXIX	homosyringic acid	0.5	3.2	nd	nd	0.2	nd	b
XXX	guaiacylpropanoic acid	1.7	2.2	5.2	nd	3.7	4.9	b
XXXI	syringylpropanoic acid	0.8	1.3	nd	nd	0.4	0.1	b
XXXII	cinnamic acid	1.2	1.9	0.8	nd	1.2	1.6	a
XXXIII	ferrulic acid	0.3	0.5	0.8	nd	0.3	0.6	a
XXXIV	sinapic acid	0.3	0.6	nd	nd	nd	nd	a

[a] μg per g of wood burned.

[b] See Figures 3.3 and 3.4. All compounds detected as TMS derivatives.

[c] Kern Wildlife Refuge, San Joaquin Valley, CA.

[d] Compound identification code: a, authentic standard; b, library match, quantification based on comparison to analogous compound.

[e] nd, not detected.

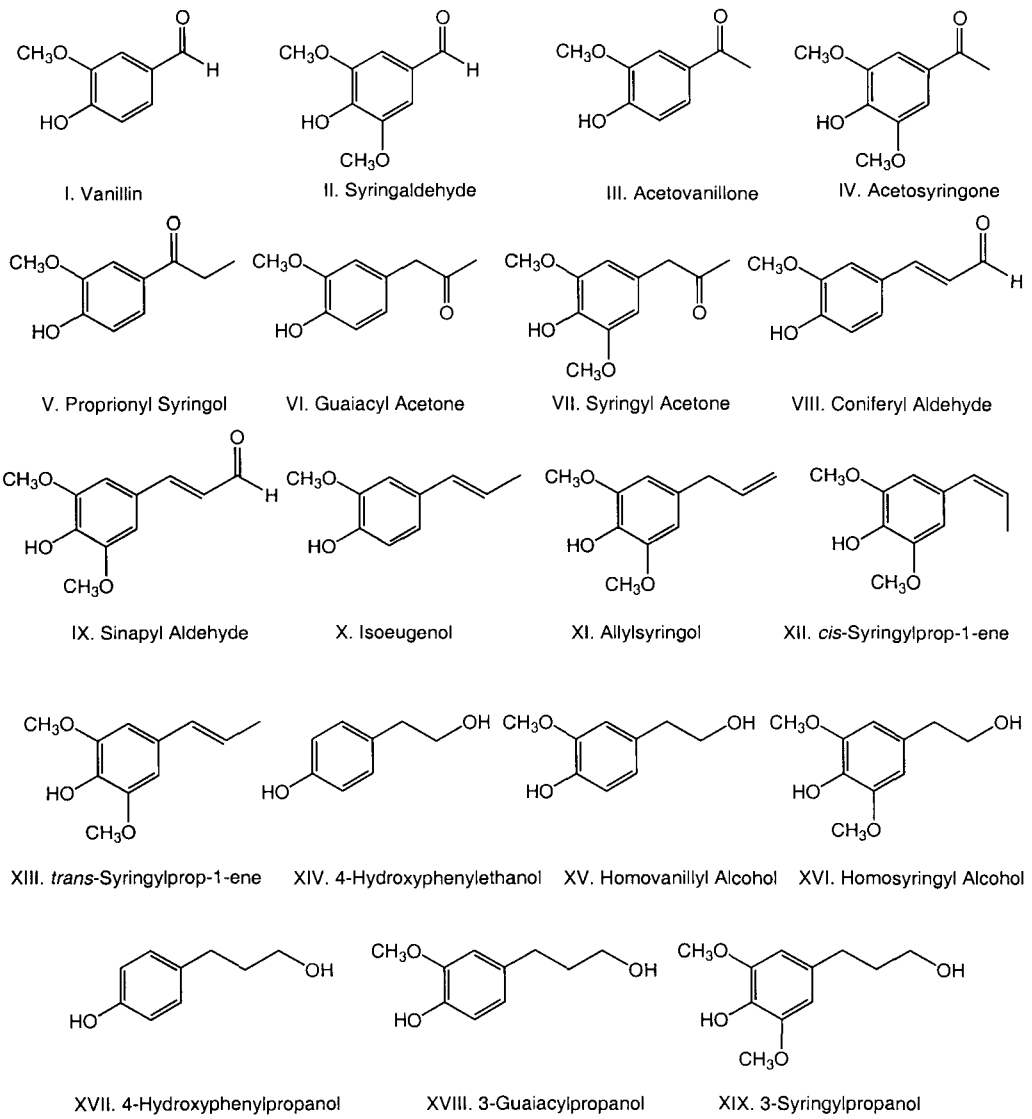

Figure 3.3: Structures of lignin breakdown products listed in Table 3.2.

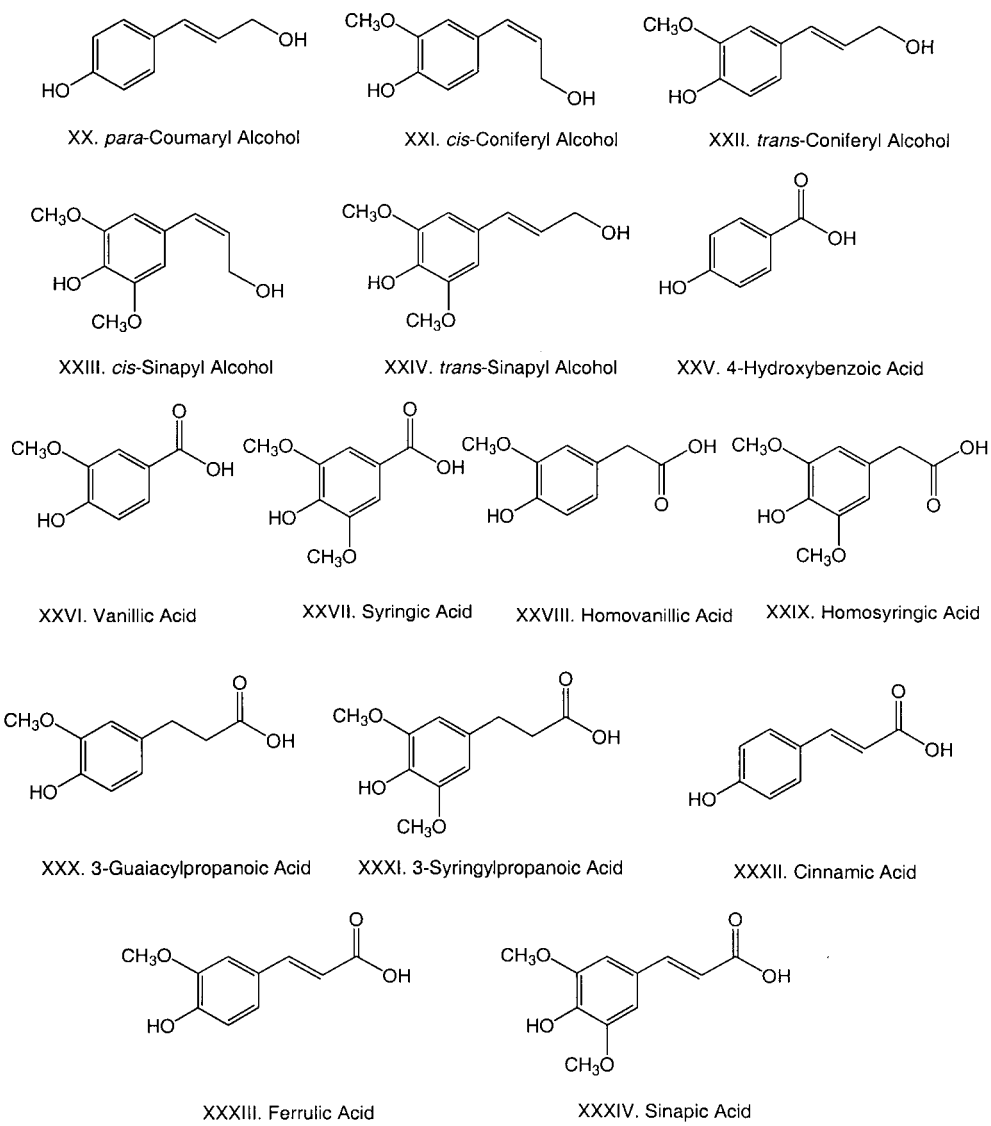

Figure 3.4: Structures of lignin breakdown products listed in Table 3.2 (continued).

from coniferyl alcohol, though lesser amounts of these are also present.

In the atmospheric sample taken at the Kern Wildlife Refuge, lignin breakdown products generally are not detected; only a few are present at very low concentrations. By contrast, many of these products are detectable in the urban atmospheric samples taken at Bakersfield and Fresno, where burning of wood in residential fireplaces is common. This suggests that these compounds are sufficiently abundant to be used as tracers for wood smoke in the urban atmosphere, though the long-term stability of these products has not yet been ascertained.

3.3.3 Lignans

In addition, several compounds tentatively identified as dimers of the lignin precursors are found in the wood smoke and in the atmosphere. Some of these dimers occur naturally in plants, while others are formed via radical recombination during combustion (34). No commercial standards for these compounds are currently available. Accordingly, their exact structures (Figure 3.5) and their quantification (Table 3.3) based on response factors for smaller but similar compounds are both uncertain. Their relatively large concentrations in both wood smoke and in the ambient samples suggests, however, that they may be developed into suitable tracers for wood smoke in atmospheric fine particulate matter if standards can be obtained in the future.

3.3.4 Alkanols and Sterols

Emission factors and atmospheric concentrations for the alcohols and the sterols are shown in Table 3.4. Normal alcohols from C_{18}–C_{30} were detected in both the wood smoke and in the atmospheric fine particulate matter samples, and lighter alcohols from C_{14}–C_{17} were also detected in the ambient samples

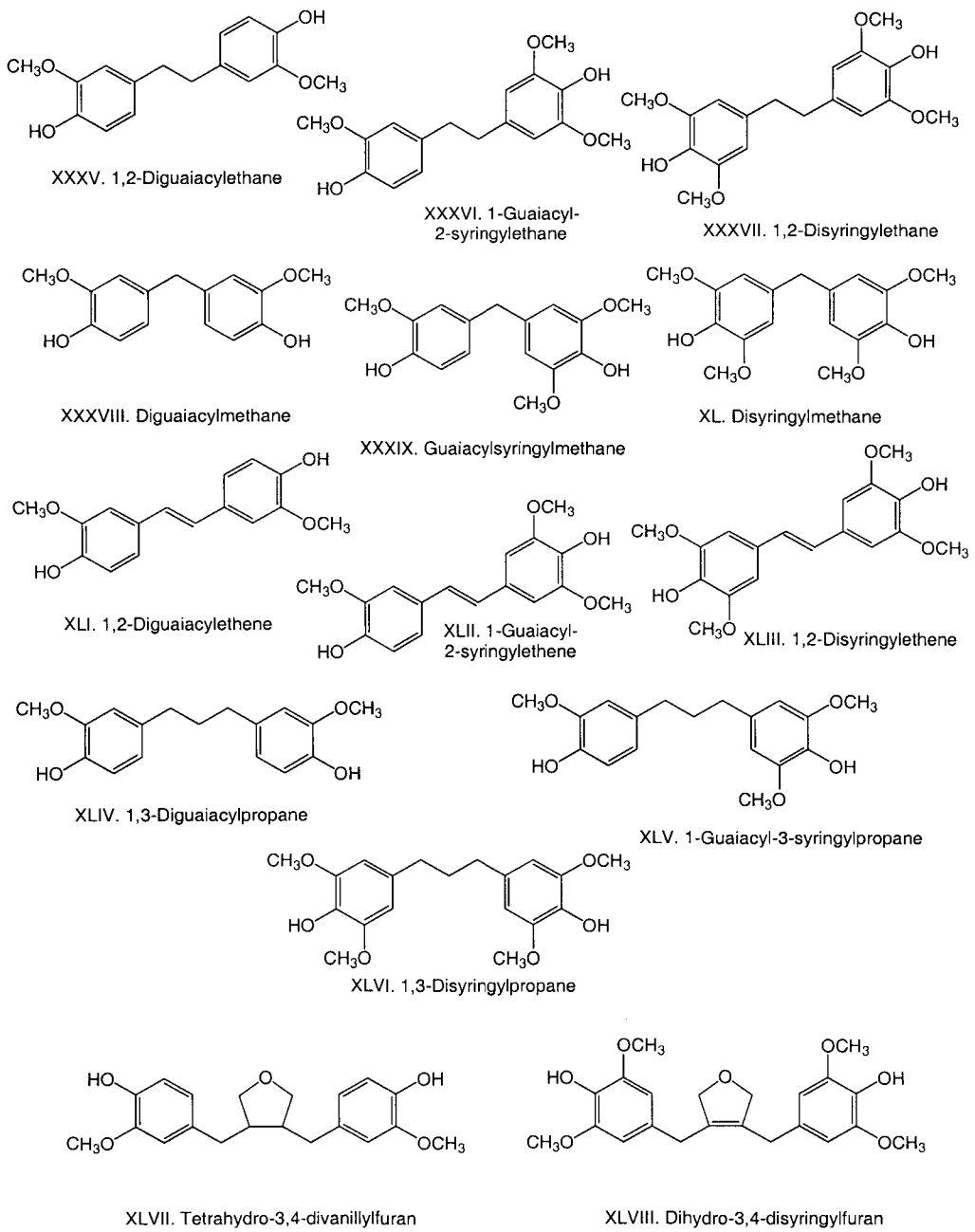

Figure 3.5: Structures of lignans and related products listed in Table 3.3.

Table 3.3: Lignans and related products detected in wood smoke and in the atmosphere of the San Joaquin Valley, California.

Structure Number[b]	Compound	Emission Factor[a]			Concentration (ng m^{-3})		
		Oak	Eucalyptus	Pine	KWR[c]	Bakersfield	Fresno
XXXV	1,2-diguaiacylethane	14.	11.	71.	0.1	39.	61.
XXXVI	1-guaiacyl-2-syringylethane	9.1	9.2	nd[d]	nd	1.4	nd
XXXVII	1,2-disyringylethane	26.	23.	nd	nd	0.6	nd
XXXVIII	diguaiacylmethane	0.6	0.9	1.3	nd	1.7	2.4
XXXIX	guaiacylsyringylmethane	0.7	1.3	nd	nd	nd	nd
XL	disyringylmethane	4.7	2.3	nd	nd	0.2	nd
XLI	1,2-diguaiacylethene	6.6	5.6	50.	nd	0.3	0.4
XLII	1-guaiacyl-2-syringylethene	1.9	0.1	nd	nd	0.1	0.1
XLIII	1,2-disyringylethene	0.6	0.2	nd	nd	0.1	0.0
XLIV	1,3-diguaiacylpropane	1.6	0.8	11.	nd	3.8	5.9
XLV	1-guaiacyl-3-syringylpropane	0.2	0.2	nd	nd	nd	nd
XLVI	1,3-disyringylpropane	0.4	0.2	nd	nd	nd	nd
XLVII	tetrahydro-3,4-divanillylfuran	0.9	0.5	4.8	nd	2.3	5.7
XLVIII	dihydro-3,4-disyringylfuran	3.8	1.4	nd	nd	0.6	nd

[a] μg per g of wood burned.

[b] All compounds detected as TMS derivatives. Structures tentatively assigned based on mass spectra and retention times; see Figure 3.5.

[c] Kern Wildlife Refuge, San Joaquin Valley, CA.

[d] Not detected.

only. A strong even to odd carbon number preference was observed in the alkanol concentrations, indicating their biological origin. Most of the alkanols are at relatively low concentrations in the wood smoke, though the C_{22}–C_{28} even carbon number alcohols were somewhat more abundant. The C_{22}–C_{28} even alcohols are relatively much more concentrated in the atmospheric samples, however, particularly hexacosanol (C_{26}). The high atmospheric concentrations of these compounds relative to their wood smoke emission factors is indicative that there are additional important sources for these compounds. One likely source is airborne vegetative detritus, as these alcohols are also present in the epicuticular waxes on plant leaves (45, 46).

Four sterols were detected in the samples studied here: β-sitosterol, cholesterol, campesterol, and stigmasterol. β-Sitosterol was the most abundant, with emission factors of 7.4–12 μg g^{-1} of wood burned and an atmo-

Table 3.4: Normal alcohols and sterols detected in wood smoke and in the atmosphere of the San Joaquin Valley, California.

	Emission Factor[a]			Concentration (ng m^{-3})			
Compound	Oak	Eucalyptus	Pine	KWR[b]	Bakersfield	Fresno	Code[c]
tetradecanol	0.2	0.4	0.3	0.6	1.4	1.1	a
pentadecanol	0.0	0.0	0.3	0.2	0.5	0.3	a
hexadecanol	0.2	0.1	0.3	0.6	1.9	1.6	a
heptadecanol	nd[d]	nd	nd	0.1	0.3	0.1	b
octadecanol	0.7	0.2	0.7	0.4	2.5	2.9	a
nonadecanol	0.0	nd	0.0	0.0	0.4	0.4	b
eicosanol	0.3	0.1	1.0	0.2	2.0	2.1	a
heneicosanol	0.1	0.0	0.0	0.1	0.8	1.1	b
docosanol	0.9	0.2	4.3	0.5	6.6	9.3	a
tricosanol	0.3	0.1	0.2	0.1	1.1	1.3	b
tetracosanol	2.9	0.7	2.9	1.6	11.9	18.	a
pentacosanol	0.4	0.1	nd	0.4	2.4	3.2	b
hexacosanol	3.1	4.1	nd	8.9	44.	61.	a
heptacosanol	0.1	nd	nd	0.3	0.8	0.6	b
octacosanol	0.1	5.9	nd	1.2	8.6	11.	a
triacontanol	nd	0.6	nd	1.2	2.4	2.3	a
cholesterol	1.6	2.2	1.7	3.5	9.9	7.0	a
campesterol	0.4	nd	nd	nd	nd	0.8	a
stigmasterol	0.6	nd	nd	nd	2.0	nd	a
β-sitosterol	9.5	12.	7.4	0.5	23.	20.	a

[a] μg per g of wood burned.

[b] Kern Wildlife Refuge, San Joaquin Valley, CA.

[c] Compound identification code: a, authentic standard; b, library match, quantification based on comparison to analogous compound.

[d] Not detected.

spheric concentration exceeding 20 ng m^{-3} in Bakersfield and Fresno. These relatively high concentrations indicate that β-sitosterol is an especially attractive candidate indicator for the possible presence of aerosol impacted by biomass burning, though noncombustion sources (e.g., plant wax detritus) may inject β-sitosterol into the atmosphere as well.

3.3.5 Alkanoic, Alkenoic, and Resin Acids

Long chain C_{14}-C_{28} normal alkanoic acids were detected as TMS esters in each of the samples studied here. In addition, the alkenoic acids $C_{16:1}$ (palmitoleic acid), $C_{18:1}$ (oleic acid), and $C_{18:2}$ (linoleic acid) were present. Several resin acids (diterpenoids) were detected in the pine smoke sample. These compounds and their concentrations have been previously quantified in these same source and atmospheric samples (27, 38, 47) and therefore are not presented in the data tables and are not discussed further here.

In summary, the sugar anhydrides galactosan and mannosan are present with levoglucosan at high concentrations in atmospheric particulate matter that is impacted by wood combustion. Several compounds derived from wood lignin are also found in the atmosphere at lower concentrations. Provided that these derivatives from lignin have a sufficiently long atmospheric lifetime such that they are conserved during transport from their combustion sources to the sampling site, they could potentially be used to distinguish between particulate matter arising from softwood and hardwood combustion. In Chapter 4, the effluents from other major fine particle sources, including meat smoke (48), vegetative detritus, and paved road dust, are examined by silylation to quantify polar organic compounds which can be used in chemical mass balance receptor modeling calculations like those of Schauer et al. (9).

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4 Highly Polar Organic Compounds Present in Fugitive Sources and in the Ambient Atmosphere

4.1 Introduction

In order to conduct organic chemical tracer-based studies of the relative contributions of different emissions sources to the fine organic particles in the atmosphere, it is necessary to characterize the source emissions profiles of each of the significant anthropogenic and biogenic sources. In addition to those sources already studied in Chapters 2 and 3, these include vegetative detritus, cigarette smoke, paved road dust, tire dust, brake dust, and motor vehicle emissions (1). Extracts of fine organic particle samples from these sources have previously been examined by gas chromatography/mass spectrometry (GC/MS) for compounds that could serve as molecular tracers for these sources (2–6). In this chapter, each of these source samples is investigated further to assess the presence of individual polar organic compounds which could potentially be used as additional tracers for these sources of atmospheric fine organic aerosol. These polar organic compounds are also sought in samples of atmospheric fine particulate matter.

4.2 Atmospheric Samples

Atmospheric fine particulate matter samples were collected daily at three sites in the San Joaquin Valley of California over 24-h periods (from noon to noon) from December 5, 1995, to January 6, 1996, as part of the State of California's IMS95 air quality study (7, 8). The atmospheric samples analyzed here were collected at the Kern Wildlife Refuge (KWR) and at urban sites in Bakersfield and Fresno, CA. Fine particle samples ($d_p < 3$ μm) were collected on 102 mm diameter prebaked quartz fiber filters (Pallflex Tissuequarts 2500 QAO) using a high volume dichotomous sampler (9) operating at a flowrate of 175 L min^{-1}. At each location, composites were formed from portions of both samples taken over the two consecutive 24-h periods from January 4–6, 1996. These samples were extracted and analyzed by GC/MS by the same methods as described below for the source samples.

4.3 Source Samples

4.3.1 Vegetative Detritus

Epicuticular waxes present on the surfaces of plant leaves can become airborne when leaves rub against each other in the wind. This vegetative detritus is a significant source of fine organic aerosol (1). A previous study of Los Angeles vegetation found that while no single compound could serve as a suitable tracer for vegetative detritus in the Los Angeles atmosphere, the high molecular weight *n*-alkanes, with their strong odd/even carbon number predominance, taken as a group provide a distinct pattern that could serve that purpose (4). However, other anthropogenic activities involving biogenic sources, such as cigarette smoking, also contribute particles containing these high molecular weight alkanes to the urban atmosphere. While it is possible

to ascertain the contribution of cigarette smoke to the urban fine organic aerosol burden using a separate unique set of tracers (5), and then apportion the contribution of leaf particle abrasion products, it would be useful to have additional compounds that are either found only in leaf particle abrasion products or that have no other significant source. To search for polar organic compounds which might serve as tracers for vegetative detritus in the urban atmosphere, extracts of fine particle abrasion products from green and dead leaf samples were silylated and analyzed by GC/MS, as discussed below.

Experimental Methods

Sample Collection. Green and dead leaves from 62 plant species were collected and composited to represent the variety of vegetation that exists in Southern California near Los Angeles (1). In separate experiments, green and dead leaves were resuspended in a Teflon bag while purified air was blown through the bag over a period of 2 h. The contents of the bag were agitated to generate particles as the leaves rubbed together and the resulting aerosol was withdrawn through cyclone separators that removed particles with aerodynamic diameters greater than 2 μm. Fine particles were collected on 47-mm quartz fiber filters (Pallflex 2500 QAO) that had been prebaked at 750 °C for at least 2 h to reduce organic contamination.

Sample Extraction and Analysis. The quartz fiber filter extraction protocol used here is described in greater detail elsewhere (4, 10). Prior to extraction, filters from each experiment were spiked with perdeuterated tetracosane (n-$C_{24}D_{50}$). The samples were then extracted with hexane (twice successively) and with benzene/isopropanol (2:1 mixture; three successive extractions) by ultrasonic agitation at room temperature for 10 minutes each

extraction. The extracts were filtered, combined, and reduced to a volume of approximately 250 μL. An aliquot of each sample was methylated by reaction with diazomethane, CH_2N_2.

In the present work, a silylating reagent consisting of bis(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) as a catalyst (Pierce Chemical Company, Rockford, IL) was used to derivatize a 5–10 μL aliquot of the sample extract, converting hydroxyl and carboxylic acid groups to trimethylsilyl (TMS) ethers and esters, respectively. Since this sample extract was previously derivatized with diazomethane, there were essentially no unreacted carboxylic acid groups remaining to be converted to TMS esters. Samples were spiked with 1,2,4-butanetriol as an internal silylation standard to verify that the derivatization was driven to completion. Upon addition of the silylating reagent (ca. 20 μL) the samples were sealed and placed in an oven at 70 °C for two hours. Within several hours after derivatization, samples were analyzed by GC/MS on a Hewlett-Packard GC/MSD (GC Model 6890; MSD model 5973) using a 30-m HP-5MS column (0.25 μm film thickness, 0.25 mm ID). The GC oven temperature programming was as follows: (1) isothermal hold at 65 °C for 10 min, (2) temperature ramp at 10 °C min^{-1} to 310 °C, and (3) isothermal hold at 310 °C for another 25 min.

Only compounds that undergo silylation are reported here, with attention focused on those compounds not previously reported for these source samples by Rogge et al. (2–5). Initial compound identification was made by matches to standard reference spectra in the Wiley and National Institute of Standards and Technology (NIST) mass spectral libraries. The compound identifications were confirmed by comparison with authentic standards, where available. In the data tables that follow, clear distinction is drawn between

those compounds positively identified and quantified via comparison to authentic standards versus those compounds tentatively identified via library matches and fundamental interpretation of the mass spectra. The mass of individual organic compounds collected on the filters was determined by replicate analysis according to the recovery of the internal standard n-$C_{24}D_{50}$, with an average precision of approximately ± 20%. For compounds with no authentic standard available, response factors were estimated from those for analogous compounds.

Results and Discussion

Alkanols. A few normal alkan-1-ols, namely those with even carbon numbers from C_{26}–C_{32}, plus C_{25}, were previously reported for these vegetative detritus sample extracts by Rogge et al. (3). Silylation enables the detection of many more alkanols present at lower concentrations. n-Alkanols ranging from C_8–C_{34} were detected in the green and dead leaf particle sample extracts. The concentrations, expressed as μg analyte per g of leaf particulate abrasion products, are given in Table 4.1, and their concentrations and mass distributions are plotted in Figure 4.1. Though the alkanols are present over a wide range of carbon numbers, their concentrations are dominated by the high even carbon numbers from C_{26}–C_{32}. For the green leaf particle sample, the maximum occurs at C_{28}. The dead leaf particle sample has generally lower amounts of alkanols than the green leaf particle sample, with the exception of C_{32}, which is more than twice as concentrated per g of vegetative detritus in the dead leaf particle sample vs. the green leaf particle sample. These quantitative results are in substantial agreement with those of Rogge et al. (3).

In addition, the secondary alkanol 10-nonacosanol is found at relatively

Table 4.1: Alkanols detected in fine particle abrasion products from green and dead leaves and in the atmosphere of the San Joaquin Valley, California.

Compound[c]	Concentration in leaf abrasion products[a]		Atmospheric Concentration[b]		
	green leaves	dead leaves	KWR[d]	Bakersfield	Fresno
1-octanol	48	16	nd[e]	0.6	nd
1-decanol	11	7.0	nd	nd	0.1
1-dodecanol	96	44	0.9	2.0	1.6
1-tridecanol	5.5	51	0.0	0.2	nd
1-tetradecanol	51	25	0.6	1.4	1.1
1-pentadecanol	5.8	30	0.2	0.5	0.3
1-hexadecanol	23	13	0.6	1.9	1.6
1-heptadecanol	0.7	1.1	0.1	0.3	0.1
1-octadecanol	28	30	0.4	2.5	2.9
1-nonadecanol	1.2	3.9	0.0	0.4	0.4
1-eicosanol	34	17	0.2	2.0	2.1
1-heneicosanol	3.8	3.7	0.1	0.8	1.1
1-docosanol	66	45	0.5	6.6	9.3
1-tricosanol	10	8.2	0.1	1.1	1.3
1-tetracosanol	470	240	1.6	12.	18.
1-pentacosanol	110	48	0.4	2.4	3.2
1-hexacosanol	13000	1900	8.9	44.	61.
1-heptacosanol	320	120	0.3	0.8	0.6
1-octacosanol	18000	4200	1.2	8.6	11.
1-nonacosanol	480	230	0.4	1.7	2.7
1-triacontanol	2100	1400	1.2	2.4	2.3
1-hentriacontanol	370	170	nd	nd	nd
1-dotriacontanol	2400	6500	nd	nd	nd
1-tritriacontanol	170	52	nd	nd	nd
1-tetratriacontanol	490	170	nd	nd	nd
10-nonacosanol	1800	1700	0.6	1.0	1.5

[a]Concentration (μg g^{-1}) in fine particulate matter released from Southern California leaf composite samples.

[b]Concentration (ng m^{-3}) measured January 4–6, 1996.

[c]All primary alkanols were positively identified by use of authentic standards and comparison of retention time and mass spectra for homologous compounds of different carbon number. 10-Nonacosanol was identified by fundamental interpretation of the mass spectrum and comparison with spectra published in the literature (11).

[d]Kern Wildlife Refuge, San Joaquin Valley, CA.

[e]Not detected.

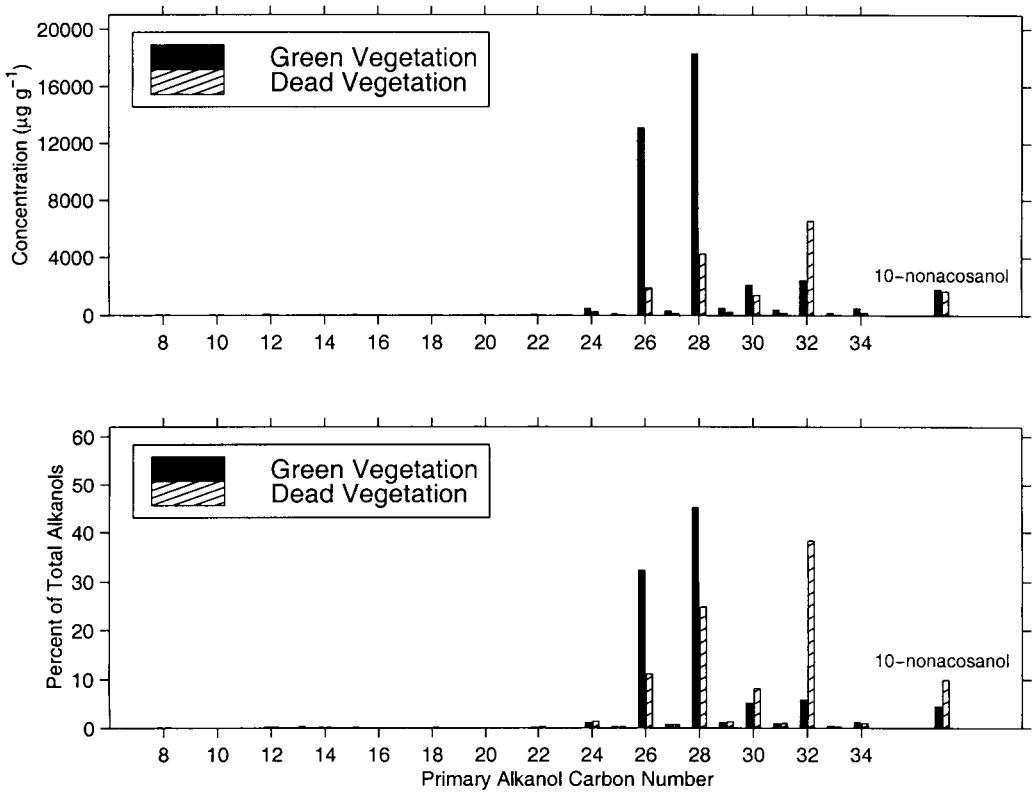

Figure 4.1: Alkanol concentrations and mass distribution in leaf abrasion products.

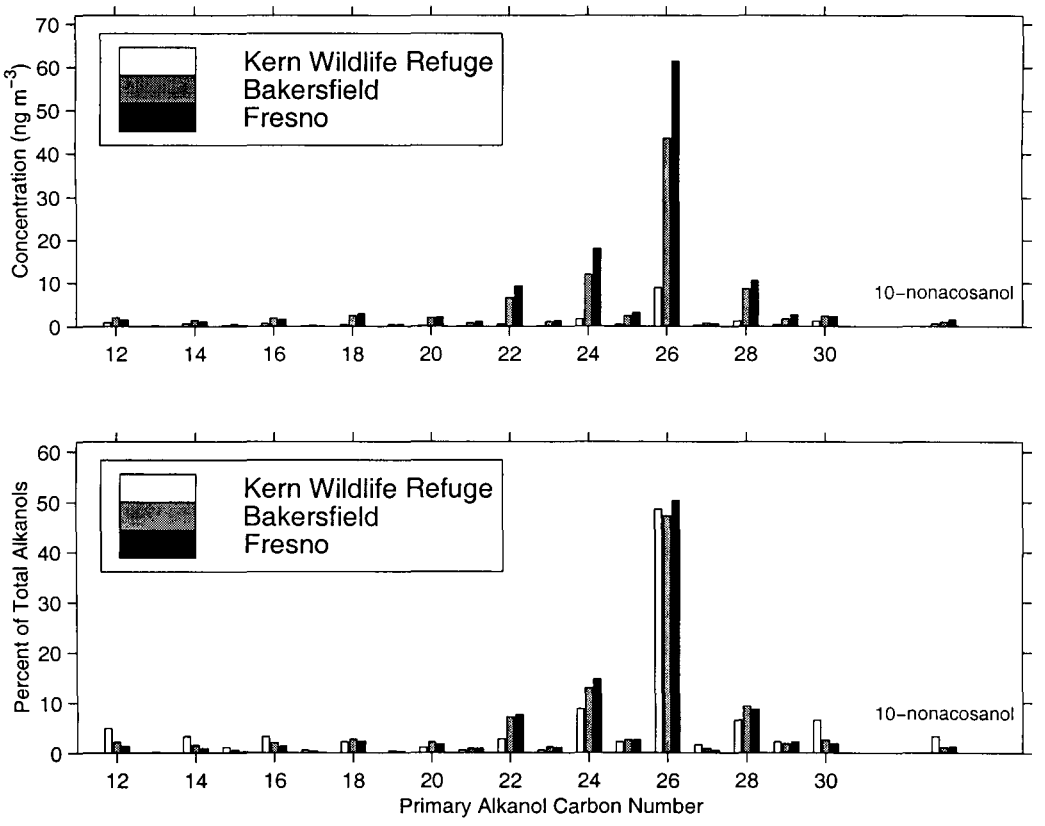

Figure 4.2: Alkanol concentrations and mass distributions in the San Joaquin Valley atmosphere.

high concentrations in the vegetative detritus samples. This compound has been reported previously as the predominant species in the epicuticular wax of leaves of hardwoods and needles from certain conifers (12–14). It is the only secondary alcohol found in these samples.

Atmospheric concentrations of alkanols in the San Joaquin Valley are also listed in Table 4.1. Figure 4.2 shows the alkanol concentrations and mass distributions at each of the three San Joaquin Valley sampling sites. As can be seen, the ambient alkanol concentrations are highest at Fresno, lower at Bakersfield, and lowest at the Kern Wildlife Refuge, indicating that

anthropogenic activity contributes to the elevated concentrations observed at the two urban sites. The alkanol concentrations are dominated by C_{26} at all sites, in contrast to the fine particulate leaf abrasion products, which peak at C_{28}. The secondary alcohol 10-nonacosanol is also found in the atmosphere at each of the sampling sites.

If organic compounds derived from vegetative detritus are conserved in the atmosphere, it is expected that their relative atmospheric concentrations would match the relative concentrations observed in the vegetation samples. However, in making this comparison it is important to realize that the vegetative detritus source samples used here are based on plant species composited in accordance with the distribution of vegetation prevailing in Los Angeles County in 1982. This vegetation profile differs from that of the San Joaquin Valley in 1996, where the atmospheric samples were taken, and thus the vegetative detritus source samples studied here probably do not represent the same leaf particle abrasion products emitted by San Joaquin Valley vegetation.

Lipid Derivatives and Sterols. Glycerol, three monoglycerides, and the sterol compounds cholesterol, campesterol, stigmasterol, and β-sitosterol are also detected as TMS ethers at low concentrations in the green and dead leaf particulate abrasion products. Their concentrations are listed in Table 4.2.

Triterpenoids. Three triterpenoid compounds are found in the fine leaf particulate matter samples. Authentic standards were not obtained for these compounds, so their identification is based on mass spectrometric data in the literature, and response factors are estimated in computing their concentrations listed in Table 4.2. The structures for these compounds are given in Figure 4.3. Four additional smaller peaks with mass spectra and retention times similar to these triterpenoids are also observed in the vegetative

Table 4.2: Organic compounds detected in fine particle abrasion products from green and dead leaves and in the atmosphere of the San Joaquin Valley, California.

Compound	Concentration in leaf abrasion products[a]		Atmospheric Concentration[b]			Code[c]
	green leaves	dead leaves	KWR[d]	Bakersfield	Fresno	
Lipids						
glycerol	20	69	4.2	28	23	a
1-palmitin	38	17	0.8	7.3	9.1	a
1-olein	4.5	4.3	nd[e]	nd	nd	a
1-stearin	15	8.4	0.5	3.1	4.0	a
Sterols						
cholesterol	83	41	3.5	9.9	7.0	a
campesterol	54	17	nd	nd	0.8	a
stigmasterol	53	49	nd	2.0	nd	a
β-sitosterol	400	86	0.5	23	20	a
Triterpenoids						
lupeol	50	13	nd	nd	nd	b
oleanolic acid	1800	260	nd	nd	nd	c
ursolic acid	2400	350	nd	nd	nd	c
other[f]	500	40	nd	nd	nd	c

[a]Concentration (μg g^{-1}) in fine particulate matter released from Southern California composite leaf samples.

[b]Concentration (ng m^{-3}) measured January 4-6, 1996.

[c]Compound identification code: a, authentic standard; b, library match, quantification based on comparison to analogous compound; c, compound class identified from literature mass spectrum.

[d]Kern Wildlife Refuge, San Joaquin Valley, CA.

[e]Not detected.

[f]Sum of four unknown triterpenoid compounds.

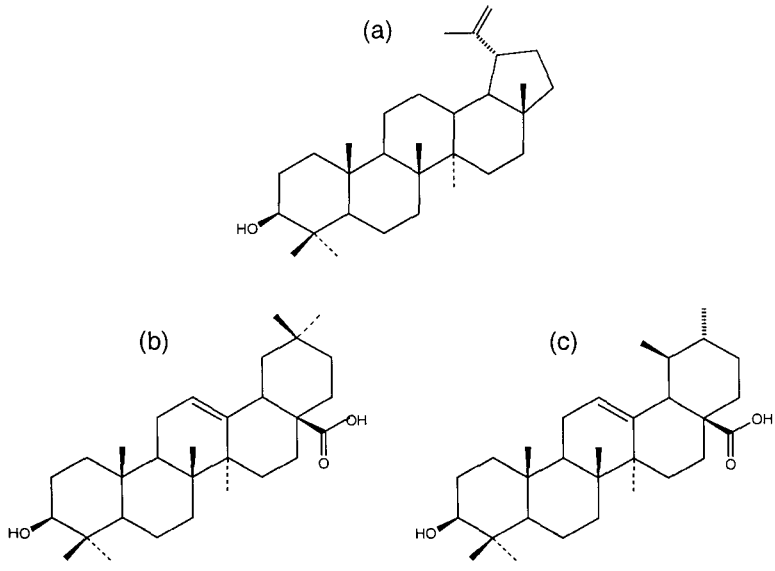

Figure 4.3: Triterpenoids detected in leaf particle abrasion products: (a) lupeol (b) oleanolic acid (c) ursolic acid.

detritus sample extracts. Their estimated concentrations are summed and reported as "other triterpenoids" in Table 4.2. The triterpenoids are found at much higher concentrations in the green leaf particle samples than in the dead leaf particle samples, possibly the result of losses due to chemical reaction between the atmosphere and the surface of the leaves, or perhaps due to microbial alteration of the triterpenoids occurring in the dead leaf matter (15). None of these triterpenoid compounds are detected in any of the San Joaquin Valley atmospheric samples, indicating that they are reactively unstable in the atmosphere. This is consistent with the observation that their concentrations are greatly depleted in the dead vegetation samples.

4.3.2 Emissions from Motor Vehicles

Motor vehicle exhaust is one of the most important sources of fine particulate matter in the polluted urban environment. Emissions inventory es-

timates and source-receptor modeling calculations have found that exhaust from heavy-duty diesel trucks and catalyst and non-catalyst gasoline-powered motor vehicles together accounted for approximately 21–49% of the annual average primary fine organic aerosol in the Los Angeles urban area in 1982 (1, 16). During a study of two wintertime air pollution episodes in California's San Joaquin Valley, including the period during which the atmospheric samples discussed in Section 4.2 were taken, motor vehicle exhaust accounted for approximately 13–22% of the primary fine organic carbon particle concentration and from 10–36% of the fine particulate mass concentration at the urban sites at Bakersfield and Fresno (8). To search for polar organic compounds which might serve as additional markers for the presence of motor vehicle emissions in the urban atmosphere, catalyst- and noncatalyst-equipped automobiles and diesel truck exhaust sample extracts were silylated and analyzed by GC/MS.

Experimental Methods

In one set of experiments, a fleet of six noncatalyst-equipped cars and seven catalyst-equipped cars were tested on dynamometers to simulate urban driving conditions. In addition, two heavy-duty diesel trucks were tested on a dynamometer with a driving cycle that included idling modes, maintaining a constant driving speed at 40 and 70 km h^{-1}, and abrupt acceleration and deceleration modes. The sampling system used was a dilution sampler, which simulates the cooling and condensing process that occurs in the atmosphere by allowing hot vapor phase organic gases to cool with dilution air and condense onto preexisting aerosol within the sampler. Large particles ($d_p > 2$ μm) were removed by AIHL cyclone separators. Fine particles were collected on prebaked 47-mm quartz fiber filters (Pallflex 2500 QAO). Fur-

ther details of the dilution sampler design and the motor vehicle sampling procedure are available elsewhere (2, 6, 17).

In a separate set of experiments, emissions from two medium-duty diesel trucks, three catalyst-equipped light-duty trucks, six catalyst-equipped automobiles, and two noncatalyst vehicles were sampled using a dilution sampling system that had been modified to capture semivolatile organic compounds (18–20). The exhaust was sampled while the vehicles were driven on a dynamometer. Fine particulate matter was collected on prebaked quartz fiber filters, backed up by a polyurethane foam plug used to capture semivolatile organic compounds volatilized from the filter during sampling.

The same quartz fiber filter extraction protocol as described above in Section 4.3.1 was used here for the motor vehicle samples. Prior to extraction, filters from each experiment were spiked with $C_{24}D_{50}$ as an internal standard, then extracted with hexane and with a benzene/isopropanol mixture. The extracts were filtered, combined, and reduced to a volume of approximately 250 μL. Sample aliquots were silylated and analyzed by GC/MS.

Results

Bulk and detailed organic analyses of the underivatized and methylated motor vehicle sample extracts have been described previously (2, 6, 19, 20). Petroleum biomarkers (i.e., hopanes and steranes) were developed as tracers for motor vehicle exhaust in the urban atmosphere, and were successfully used to apportion the contribution of motor vehicle exhaust to ambient fine particulate matter concentrations (8, 16). It was expected that silylation would enable the detection of some additional oxygenated products in vehicle exhaust that were not measurable by previous methods. However, no significant TMS compounds were evident in any of the silylated motor vehi-

cle extracts other than those compounds (mainly alkanoic acids, alkanedioic acids, and some aromatic acids) that were previously quantified as methyl esters.

4.3.3 Brake Dust

Tailpipe emissions from trucks and automobiles are one of the most obvious sources of air pollution in urban environments. However, particulate matter emitted to the atmosphere due to motor vehicle traffic has several emissions sources in addition to tailpipe exhaust. One such source is the particulate dust from the wearing of brake lining materials, which in 1982 was estimated to be comparable in magnitude to the emissions from catalyst-equipped gasoline-powered vehicles (1). To search for polar organic compounds which might serve as tracers for brake dust and hence motor vehicle traffic in the urban atmosphere, a brake dust sample extract was silylated and analyzed by GC/MS.

Experimental Methods

Brake dust particles were collected from the rear drum brakes of a single late-model light truck. This dust was resuspended in a Teflon bag and sampled in a manner similar to that used for the leaf particle samples. Contents of the bag were drawn through cyclone separators that removed particles larger than 2 μm in aerodynamic diameter, and fine particles were collected on prebaked 47-mm quartz fiber filters. Further details of the brake dust source sampling protocol are given by Hildemann et al. (1).

The brake dust sample was extracted in the same manner as described for the vegetative detritus samples. The filters were spiked with perdeuterated tetracosane (n-$C_{24}D_{50}$), and extracted twice with hexane and three times with a 2:1 mixture of benzene/isopropanol. The extracts were filtered, com-

bined, and reduced to a volume of approximately 250 μL. An aliquot of the sample was methylated by reaction with diazomethane. In the present work, a 5–10 μL aliquot of the methylated sample extract was silylated and analyzed by GC/MS in the same manner as the leaf particle sample extracts discussed above.

Results and Discussion

This same brake dust sample was previously analyzed by Rogge et al. (3) without using the technique of silylation. The principal organic compounds in brake dust by mass reported in that research included alkanoic acids and polyethylene glycol alkyl ethers. Though the alkanoic acids are also detectable by silylation, they are not reported here because they are easily detected as methyl esters. The focus here is on compounds whose detection is made possible or is greatly improved by silylation.

Figure 4.4a shows the GC single-ion chromatogram (m/z = 135) from the silylated brake dust sample extract. Each of the four peaks evident in the chromatogram has a very similar mass spectrum; the mass spectrum corresponding to the peak labelled B is given in Figure 4.4b. The TMS derivatives of polyethylene glycol methyl ethers and polyethylene glycol ethyl ethers have characteristic peaks at m/z = 73, 75, 89, 103, M-15, and M, where M is the parent molecular ion. The compounds in Figure 4.4 have a very different mass spectrum, with repeating pairs of ions two mass units apart, each pair separated by 30 mass units from the next pair. The intervals of 30 mass units almost certainly arise from -CH_2O groups. These compounds remain unidentified, but their spectra are inconsistent with their being polyethylene glycols, the -CH_2CH_2O groups of which should yield peaks separated by 44 mass units. None of the compounds in Figure 4.4 are detected in any of the

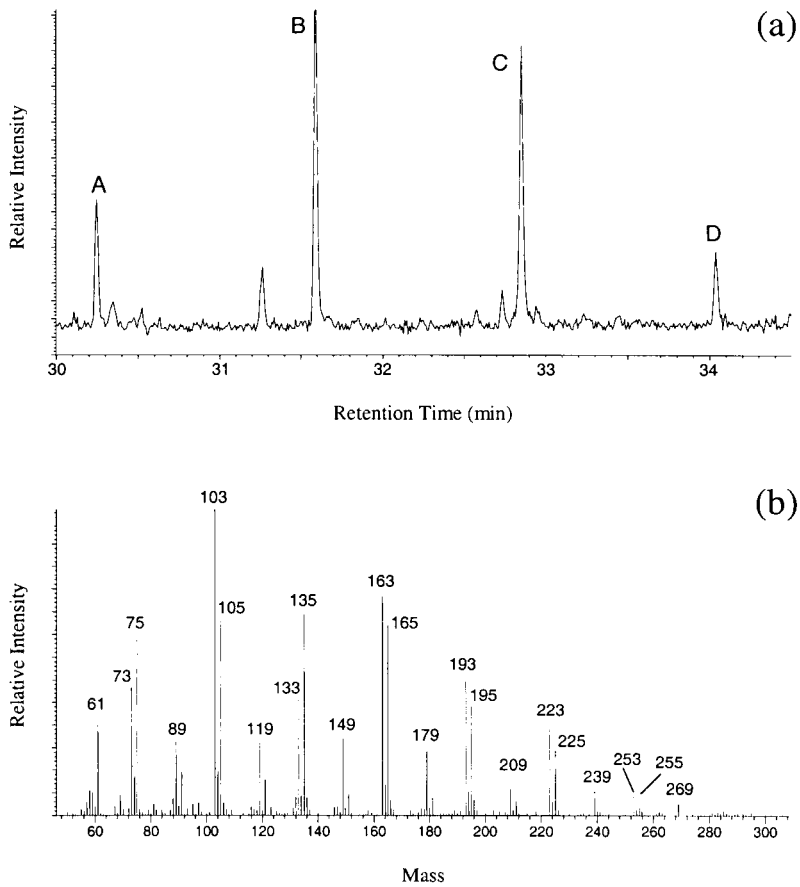

Figure 4.4: Unknown homologous series of compounds detected in brake dust. (a) Single-ion mass fragmentogram (m/z = 135) and (b) mass spectrum from peak B, which is characteristic of each of the four peaks A–D labelled in (a).

San Joaquin Valley atmospheric samples.

4.3.4 Tire Wear Particles

Another non-tailpipe vehicular source of organic particulate matter emissions to the urban atmosphere is the wearing and abrasion of tires. In 1982 tire debris was estimated to contribute 1.4% of the total fine aerosol organic carbon emissions within the Los Angeles urban area (1). To search for polar organic compounds which might serve as tracers for tire debris and hence motor vehicle traffic in the urban atmosphere, a tire dust sample was silylated and analyzed by GC/MS.

Experimental Methods

To obtain a characteristic sample of the chemical composition of tire particulate matter, a used radial tire (195/60R-15 Toyo, 7200 miles) was run on a rolling resistance testing machine at a tire testing laboratory. The tire wear particles that accumulated on the surfaces of the testing machine were collected as a grab sample. Attempts to size-segregate the fine tire particles were unsuccessful, as when the tire particles were resuspended they became electrically charged and adhered to the walls of the sampling equipment. Accordingly, a total particle sample was used instead. Since tire tread is a well-mixed industrial material, it is expected that there will be no significant differences in chemical composition between the fine and coarse fractions of tire particles. Further details of the tire debris source sampling protocol are given by Hildemann et al. (1).

The tire dust sample was extracted in the same manner as described for the vegetative detritus and brake dust samples. The filters were spiked with perdeuterated tetracosane (n-$C_{24}D_{50}$), and extracted twice with hexane and three times with a 2:1 mixture of benzene/isopropanol. The extracts were

filtered, combined, and reduced to a volume of approximately 250 μL. An aliquot of the sample was methylated by reaction with diazomethane. In the present work, 5–10 μL aliquots of the neutral and methylated sample extracts were silylated and analyzed by GC/MS in the same manner as the leaf particle and brake dust sample extracts discussed above.

Results and Discussion

This same tire dust sample was previously analyzed by Rogge et al. (3) without using the technique of silylation. The principal organic compounds in tire dust by mass reported in that research included alkanes and alkanoic acids, followed by resin acids. Resin acids are natural products found in pine tars, which are additives used by manufacturers to give tires certain desirable properties (3).

The alkanoic acids are detected as TMS esters in the silylated sample extracts, but will not be further discussed here as these compounds have been quantified previously by Rogge et al. (3). Silylation enables the detection of a few additional resin acids besides those reported by Rogge et al. Resin acid concentrations found in the tire particle extracts and in atmospheric fine particulate matter are given in Table 4.3. Chemical structures for these compounds are provided in Figure 4.5. The resin acids numbered I–V in Table 4.3 are all natural unaltered products found in pine tars. By contrast, the compounds numbered VI–IX are dihydro resin acids, which are not natural products but are chemically hydrogenated before being added during the manufacturing process. Accordingly, these compounds have the potential to be used to distinguish tire debris from wood smoke in atmospheric particulate matter, as wood smoke contains the natural resin acids but not the hydrogenated products. These markers are either not detectable at all or are

Table 4.3: Resin acids detected in tire dust and in the atmosphere of the San Joaquin Valley, California.

		sample concentrations[a]				
Compound structure and name[b]		tire dust	KWR[c]	Bakersfield	Fresno	code[d]
I	dehydroabietic acid	2300	0.6	30	79	a
II	abietic acid	280	nd[e]	1.1	1.6	a
III	7-oxodehydroabietic acid	8	nd	0.7	1.9	b
IV	pimaric acid	85	nd	6.9	17	a
V	isopimaric acid	160	0.2	10	22	a
VI	pimar-8-en-18-oic acid	310	nd	nd	nd	b
VII	isopimar-8-en-18-oic acid	560	nd	nd	nd	b
VIII	13β(H)-abiet-8-en-18-oic acid	380	nd	nd	0.2	b
IX	13α(H)-abiet-8-en-18-oic acid	1600	nd	+[f]	0.2	b

[a]Concentration in tire dust measured as μg g^{-1} in total (fine + coarse) particulate matter sampled from a single used Toyo passenger tire. Atmospheric fine particulate matter concentrations (ng m^{-3}) measured January 4–6, 1996.

[b]See Figure 4.5 for corresponding structures.

[c]Kern Wildlife Refuge, San Joaquin Valley, CA.

[d]Compound identification code: a, authentic standard; b, library match, quantification based on comparison to analogous compound.

[e]Not detected.

[f]Detected but not quantified.

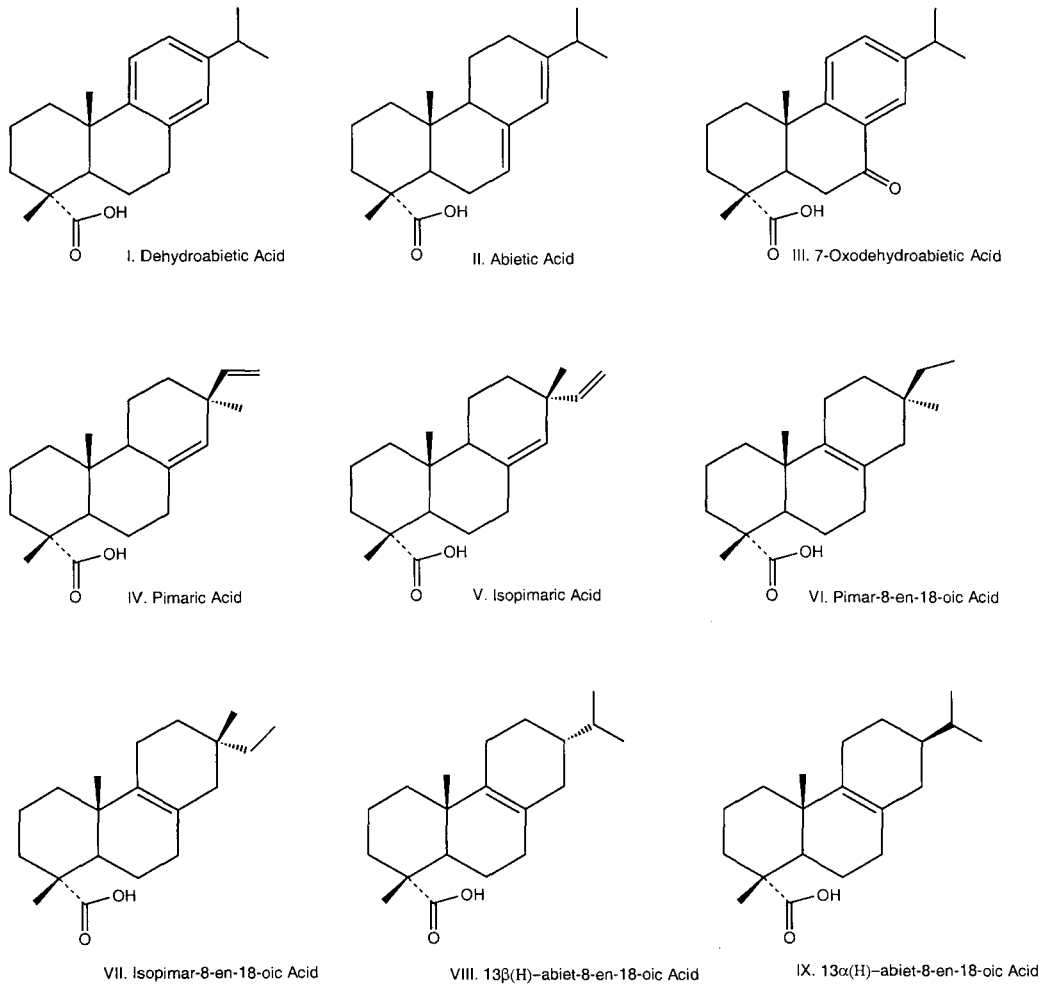

Figure 4.5: Chemical structures of resin acids detected in tire debris particulate matter. See Table 4.3.

found only at very low concentrations in the San Joaquin Valley atmospheric fine particulate matter samples studied here.

4.3.5 Paved Road Dust

In addition to the tailpipe emissions from trucks and automobiles, motor vehicle traffic causes the introduction into the atmosphere of large quantities of organic particles from the resuspension of road dust. Paved road dust is the third largest source of fine organic particulate matter emissions to the urban atmosphere, following motor vehicle exhaust and meat cooking emissions (1). A diverse array of sources contribute to fine particulate road dust. Dirt that is tracked onto roads, leaves and other plant matter that accumulate on road surfaces and are crushed by the passing traffic, and particles worn from brake linings and tires, as discussed above, all contribute to paved road dust. In addition, any other fine particles present in the atmosphere that are deposited onto road surfaces can be reentrained into the atmosphere by passing traffic or blown by wind. To search for polar organic compounds which might be used as tracers for paved road dust in the urban atmosphere, a paved road dust sample was collected and analyzed by GC/MS.

Experimental Methods

Paved road dust was collected from several residential streets in the Pasadena, CA, area using a small vacuum sweeper truck (1). Using the same procedure as was used for the leaf particle samples discussed in Section 4.3.1, the road dust was resuspended in a Teflon bag and fine particles were selected using a cyclone separator that removed particles larger than 2 μm in aerodynamic diameter. Further details of the paved road dust source sampling protocol are given by Hildemann et al. (1).

The road dust sample was extracted in the same manner as described for

the vegetative detritus, brake dust, and tire samples. The filters were spiked with perdeuterated tetracosane (n-$C_{24}D_{50}$), and extracted twice with hexane and three times with a 2:1 mixture of benzene/isopropanol. The extracts were filtered, combined, and reduced to a volume of approximately 250 μL. An aliquot of the sample was methylated by reaction with diazomethane. In the present work, 5–10 μL aliquots of the neutral and methylated sample extracts were silylated and analyzed by GC/MS in the same manner as the leaf particle, brake dust, and tire dust sample extracts as discussed above in Sections 4.3.1, 4.3.3, and 4.3.4.

Results and Discussion

Alkanols. This same fine particulate road dust sample has been examined previously by Rogge et al. (3), who reported that the major organic constituents were the alkanoic acids and alkanes. Only two alcohol compounds, C_{26} and C_{28}, were detected. In the silylated road dust sample analyzed here, the same series of n-alkanols is evident as is found in the leaf particle sample in Section 4.3.1. The concentration distribution of the alkanols in the road dust is shown in Figure 4.6. As can be seen by comparing with Figure 4.1, the road dust has a similar alkanol concentration profile to the vegetation sample, dominated by the even carbon numbers from C_{24}–C_{32}. The concentrations (μg g^{-1} of dust or leaf particles) of alkanols in the road dust are lower than the concentrations seen in the leaf particles, but because road dust is a much stronger source of atmospheric fine organic carbon emissions, the contribution of road dust to the atmospheric concentration of alkanols may be comparable to or greater than the amount emitted by the mechanical abrasion of vegetation.

Monoglycerides and Sterols. Certain monoglycerides and sterols are also

Table 4.4: Alkanols detected in fine particulate paved road dust.

Compound[a]	Concentration in paved road dust (μg g^{-1})[b]
1-octanol	nd[c]
1-decanol	10
1-dodecanol	6.3
1-tridecanol	1.7
1-tetradecanol	3.6
1-pentadecanol	2.1
1-hexadecanol	2.4
1-heptadecanol	1.4
1-octadecanol	4.3
1-nonadecanol	0.6
1-eicosanol	2.1
1-heneicosanol	0.8
1-docosanol	6.0
1-tricosanol	1.7
1-tetracosanol	22
1-pentacosanol	3.8
1-hexacosanol	67
1-heptacosanol	6.5
1-octacosanol	130
1-nonacosanol	6.4
1-triacontanol	64
1-hentriacontanol	2.0
1-dotriacontanol	25
1-tritriacontanol	0.7
1-tetratriacontanol	2.2
10-nonacosanol	74

[a]See footnote in Table 4.1.
[b]Fine particulate road dust collected from Pasadena residential streets, 1988.
[c]Not detected.

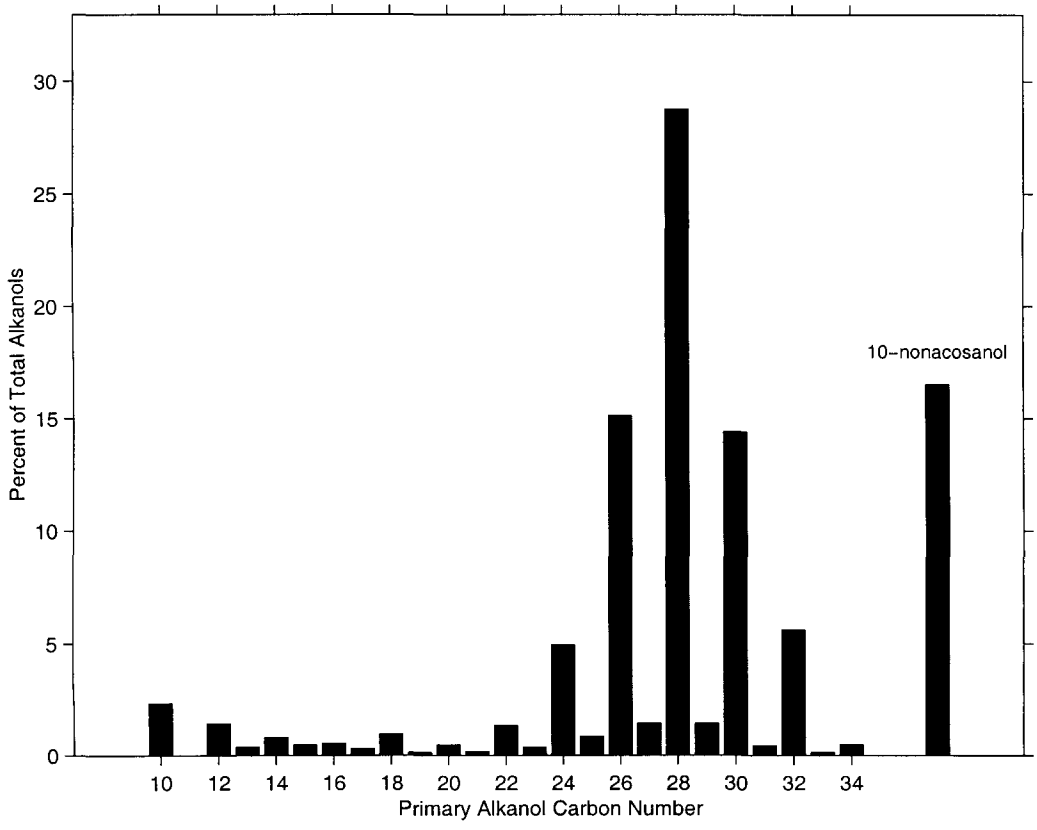

Figure 4.6: Alkanol mass distribution in Pasadena, CA, paved road dust.

Table 4.5: Monoglycerides and sterols detected in fine particulate road dust.

Compound[a]	Concentration in paved road dust (μg g^{-1})[b]
glycerol	5.4
1-palmitin	6.3
1-olein	13
1-stearin	2.3
cholesterol	5.2
β-sitosterol	14

[a]All compounds listed positively identified by use of authentic standards.
[b]Fine particulate road dust collected from Pasadena, CA, residential streets, 1988.

found in the road dust sample, and their concentrations are listed in Table 4.5. All of the compounds listed in Table 4.5, with the exception of β-sitosterol, are detected in meat smoke, as discussed in Chapter 2. However, two of the monoglycerides that are found in meat smoke, 1-myristin and 2-palmitin, are not present in the road dust. Moreover, the unsaturated monoglyceride 1-olein is present at a higher concentration than any of the saturated monoglycerides, in contrast to the situation in meat smoke. As noted previously, however, 1-olein is not found in the atmosphere, indicating that it is not chemically stable in the outdoor environment. β-Sitosterol, a plant sterol found in wood smoke and in the leaf particulate matter, is also found in the road dust. However, campesterol and stigmasterol, the other two plant sterols found in the vegetative detritus sample, are not detectable in the paved road dust.

Resin Acids. Certain of the resin acids found in tire dust and in pine wood smoke are also detected in the present road dust sample. These compound concentrations are listed in Table 4.6.

Levoglucosan. Since paved road dust is partially comprised of atmospheric

Table 4.6: Resin acids in fine particulate paved road dust.

Compound[a]	Concentration in paved road dust (μg g^{-1})[b]
dehydroabietic acid	30
abietic acid	nd[c]
7-oxodehydroabietic acid	0.7
8,15-pimaradien-18-oic acid	7.8
isopimaric acid	4.1
pimar-8-en-18-oic acid	2.8
isopimar-8-en-18-oic acid	1.4
13β(H)-abiet-8-en-18-oic acid	2.7
13α(H)-abiet-8-en-18-oic acid	8.4

[a]See Figure 4.5 for compound structures.
[b]Fine particulate road dust collected from Pasadena, CA, residential streets, 1988.
[c]Not detected.

particles that have been deposited to the road surface, any particulate organic compound found in the atmosphere might be expected to be detectable in road dust. Levoglucosan, a product of cellulose combustion found at high levels in wood smoke, is often the most abundant particle phase organic compound in the atmosphere and is present in the atmosphere at concentrations frequently exceeding 2 μg m^{-3} (see Chapter 3) and sometimes reaching levels over 7 μg m^{-3} (8). A search was conducted to determine whether or not levoglucosan was present in the Pasadena paved road dust sample, but it was not found. The road dust sample was collected during the month of May. As fireplace burning of wood is a very seasonal activity in Pasadena, it is likely that atmospheric levoglucosan concentrations were low at that time, which would explain why it is not found in the road dust.

4.3.6 Cigarette Smoke

A large amount of research has been conducted on cigarette smoke, particularly focused on the effects on the smoker and to others exposed to tobacco smoke in indoor environments. However, cigarette smoking also contributes small amounts of fine organic aerosol to the outdoor urban environment. Emissions inventory estimates and source-receptor modeling calculations have estimated that cigarette smoke accounted for approximately 0.7–2.7% of the emissions of fine organic particulate matter in the Los Angeles urban area in 1982 (6, 16). The series of high molecular weight isoalkanes and anteisoalkanes are useful markers for tobacco smoke in the atmosphere, and have been used successfully to trace cigarette smoke in several urban applications (8, 16, 21). To seek additional polar organic compounds which might be useful as tracers for cigarette smoke in the urban atmosphere, and to determine the extent to which cigarettes emit compounds that are under consideration as tracers for wood smoke or leaf particulate matter, cigarette smoke sample extracts were silylated and analyzed by GC/MS.

Experimental Methods

Two of each of six different types of cigarettes, chosen to represent a market share average of the cigarettes sold in the United States in the mid-1990s, were smoked by the same person in separate experiments (20). The cigarettes were smoked inside of a chamber designed to ensure that all of the exhaled mainstream smoke, as well as the sidestream smoke emitted during the smoldering period between puffs, entered the dilution sampler. The smoke was then passed through cyclone separators operating at a 1.8 μm size cut and collected on prebaked quartz fiber filters followed by polyurethane foam plugs. The filters from each experiment were combined into a com-

Table 4.7: Alkanols in fine particulate cigarette smoke.

Compound[a]	Cigarette smoking emission factor (μg per cigarette)
hexadecanol	0.7
octadecanol	0.6
eicosanol	2.2
heneicosanol	0.9
docosanol	6.8
tricosanol	0.6
tetracosanol	1.1
pentacosanol	1.0
hexacosanol	2.3
heptacosanol	1.8
octacosanol	10
nonacosanol	6.5
triacontanol	21
dotriacontanol	17
tetratriacontanol	2.3
10-nonacosanol	nd[b]

[a]See footnote to Table 4.1.
[b]Not detected.

posite sample, which was extracted and analyzed by GC/MS. In the present work, an aliquot of the cigarette composite sample extract is silylated to look for additional polar organic compounds present in the cigarette smoke fine particulate matter.

Results and Discussion

Alkanols. Alkanol emission factors from cigarette smoking are listed in Table 4.7. Figure 4.7 shows the alkanol emissions profile for cigarette smoking in comparison to the distribution of alkanols observed in the leaf particulate matter samples discussed in Section 4.3.1. As can be seen from Figure 4.7,

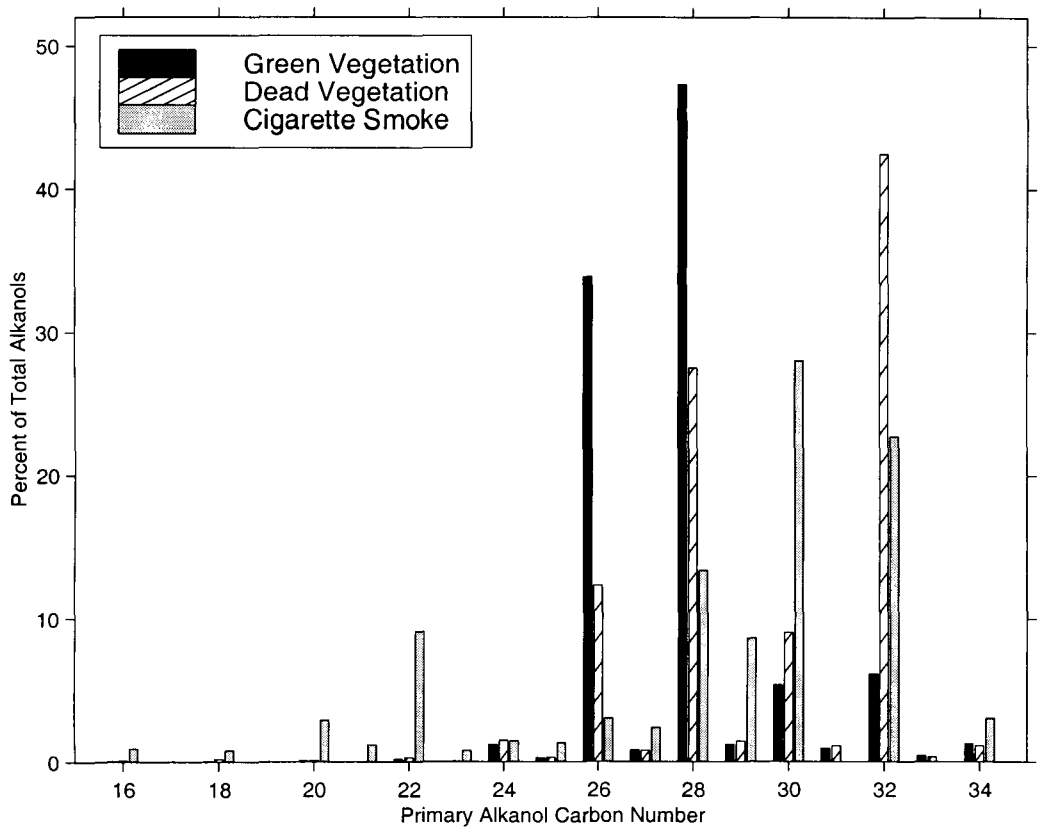

Figure 4.7: Comparison of the alkanol distributions in fine particulate cigarette smoke with fine particulate leaf abrasion products from green and dead leaves.

concentrations of C_{26} and C_{28} alcohols are relatively low in cigarette smoke compared to the green and dead vegetation samples. By contrast, the concentrations of the lower molecular weight alcohols C_{20} and C_{22} as well as the higher molecular weight alcohols at C_{30} and C_{32} are enriched relative to those observed in the particulate leaf samples.

Sugars. Sugar and sugar anhydride emission factors are listed in Table 4.8. Levoglucosan, formed during the combustion of cellulose (see Chapter 3), is emitted at over 300 μg per cigarette, making it one of the most abundant single organic compounds identified in the cigarette smoke. Galactosan and mannosan, isomers of levoglucosan, are found at concentrations an order of magnitude lower than levoglucosan, though still higher than for most other compounds found in the smoke. Erythrose, a four-carbon sugar not found in any of the three wood smoke samples examined in Chapter 3, is also present in the cigarette smoke.

Glycerol and Monoglycerides. Also listed in Table 4.8 are emission factors for glycerol and three monoglycerides. Glycerol is emitted at a rate of nearly 1 mg per cigarette, making it the second most abundant single organic compound identified in cigarette smoke, after nicotine. The three monoglycerides detected in the cigarette smoke are also emitted during meat cooking, as discussed in Chapter 2. The other monoglycerides reported in the meat smoke emissions, however, are not found in the cigarette smoke.

Phytosterols and Terpenoids. Emission factors for five phytosterols, plus cholesterol and the triterpenoid compound β-amyrin, are given in Table 4.8. Campesterol and stigmasterol are much more abundant relative to β-sitosterol in the cigarette smoke than they are in the wood smoke (Table 3.4) and in the particulate leaf samples (Table 4.2).

Lignin Breakdown Products. A few of the lignin breakdown products

Table 4.8: Polar organic compounds in fine particulate cigarette smoke.

Compound	Cigarette smoking emission factor (μg per cigarette)	Code[a]
Sugars		
galactosan	31	a
mannosan	11	a
levoglucosan	310	a
erythrose	18	b
sucrose	10	a
maltose	23	b
Glycerol and Monoglycerides		
glycerol	980	a
1-palmitin	6.9	a
1-olein	3.5	a
1-stearin	2.1	a
Sterols and Terpenoids		
cholesterol	5.5	a
campesterol	20	a
stigmasterol	17	a
β-sitosterol	33	a
stigmastadienol	12	b
cycloartanol	3.2	b
β-amyrin	5.5	b

[a]Compound identification code: a, authentic standard; b, library match, quantification based on comparison to analogous compound.

Table 4.9: Polar organic compounds in fine particulate cigarette smoke.

Compound	Cigarette smoking emission factor (μg per cigarette)	Code[a]
Lignin-derived compounds		
hydroxyphenylethanol	33	a
coniferyl alcohol	20	b
sinapyl alcohol	4.8	b
4-hydroxybenzoic acid	16	b
vanillic acid	3.9	a
syringic acid	2.0	a
Other compounds		
dehydroabietic acid	1.5	a
trihydroxypropanoic acid	8.2	b
dihydroxyfuranone[b]	7.8	b
inositol	610	b
β-tocopherol	20	c
α-tocopherol (vitamin E)	160	c

[a]Compound identification code: a, authentic standard; b, library match, quantification based on comparison to analogous compound; c, compound tentatively identified from mass spectrum.

[b]Sum of two peaks with the same mass spectrum.

found in wood smoke are also detected in the cigarette smoke. Emission factors of these compounds, three alcohols and three acids, are listed in Table 4.9.

Other Compounds. Emission factors for other miscellaneous compounds found in the cigarette smoke are also provided in Table 4.9. Most noteworthy among these is inositol, a six-carbon alditol (i.e., cyclohexane with a hydroxy group attached to each member of the ring). This compound is emitted at a rate of over 600 μg per cigarette, nearly as high as the emission factor of glycerol. In contrast to glycerol, however, which is frequently detected in

other source samples as well as atmospheric samples, inositol is not found in any of the other source samples studied here, nor is it detectable in any of the San Joaquin Valley atmospheric samples.

4.4 Source Apportionment of Polar Organic Compounds in the San Joaquin Valley Atmosphere

A chemical mass balance (CMB) receptor model that uses organic compounds as tracers for the sources has been developed and applied to determine the source contributions to atmospheric pollutant concentrations during two 48-h high pollution episodes that occurred in California's San Joaquin Valley in December 1995–January 1996 (8, 16). In a CMB model, a mass balance is constructed in which the concentration of a particular chemical entity in a given ambient sample is expressed as a linear combination of the contributions from the various sources:

$$c_{ik} = \sum_{j=1}^{m} a_{ij} s_{jk} \qquad i = 1, 2, \ldots \ n.$$

where c_{ik} is the atmospheric concentration of chemical species i at receptor site k, s_{jk} is the unknown total particulate mass contribution of source j to site k, and a_{ij} is the fraction of chemical species i present in the emissions of source j. The above system of equations assumes that there is no selective loss or gain of any of the chemical species during transport from the sources to the receptor sites, and also that the m sources completely account for all the species in the model. In this section, the source apportionment results of Schauer and Cass (8) for the January 4–6, 1996, episode are used with the emission factors determined in Chapters 2 and 3 and in Section 4.3 to predict the ambient concentrations of certain polar organic compounds, and these predictions are compared to observations.

Table 4.10: Source apportionment of fine particulate mass concentrations in the San Joaquin Valley, January 4–6, 1996, as determined by chemical mass balance.[a]

Source	Bakersfield	Fresno	Kern Wildlife Refuge
hardwood combustion	5.68		
softwood combustion	4.46		
combined wood combustion[b]		14.7	0.16
diesel exhaust	5.32	5.15	1.75
gasoline powered vehicle exhaust	1.73	1.10	0[c]
meat cooking	3.50	1.51	0[c]
paved road dust	0.55	1.00	0[c]
natural gas combustion	0.43	0[c]	0[c]
vegetative detritus	0[c]	0[c]	1.13
organics (other + secondary)	4.06	4.15	4.46
sulfate (secondary + background)	2.99	2.80	2.07
secondary nitrate	15.4	18.9	14.2
secondary ammonium ion	5.29	5.49	4.13
sum of identified sources	49.4	54.8	28.0
measured	52.1	55.3	33.5

[a]Adapted from Schauer and Cass (8).

[b]Hardwood and softwood combustion were lumped together at Fresno and Kern Wildlife Refuge for this sampling period.

[c]Not statistically different from zero with greater than 95% confidence and therefore removed from CMB model.

The atmospheric fine particle concentration increments due to nine primary sources of fine organic aerosol emissions in California's San Joaquin Valley as calculated by the receptor modeling procedure of Schauer and Cass (8) are listed in Table 4.10. The alcohol and sterol emission profiles for meat smoke, wood smoke, vegetative detritus, and paved road dust sources developed in the present work are scaled according to the attributed fine particle mass concentrations for each of these source types and then summed to compute the predicted ambient concentrations for individual alcohols and sterols, as shown in Figures 4.8 and 4.9. As can be seen in Figure 4.8, the CMB model significantly underpredicts the alkanol concentrations at the urban sites Bakersfield and Fresno. This is to be expected, as vegetative detritus, the strongest source of the alkanols, was excluded by Schauer and Cass (8) from the model for those two sites because the vegetation tracers previously available for use in the model were present in very low concentrations, near or below detection limits in the atmospheric samples. In the future, use of the alkanols as species in the CMB model might result in a nonzero amount of the fine organic aerosol at Bakersfield and Fresno being apportioned to leaf particulate abrasion products.

The agreement between the predicted and measured alkanol concentrations, however, is better at the Kern Wildlife Refuge, which does have a small component of vegetation contributing to its fine aerosol burden. Good agreement between model predictions and observations are seen at C_{26}, C_{27}, C_{29}, and C_{30}, but C_{28} is greatly depleted in the atmosphere relative to its concentration predicted by the CMB model. As noted in Figures 4.1 and 4.2, the atmospheric alkanol concentrations peak at C_{26}, in contrast to the vegetation samples, which peak at C_{28}. Alkanols above C_{30} are not found in the atmospheric samples, but this may be due to the fact that analytical de-

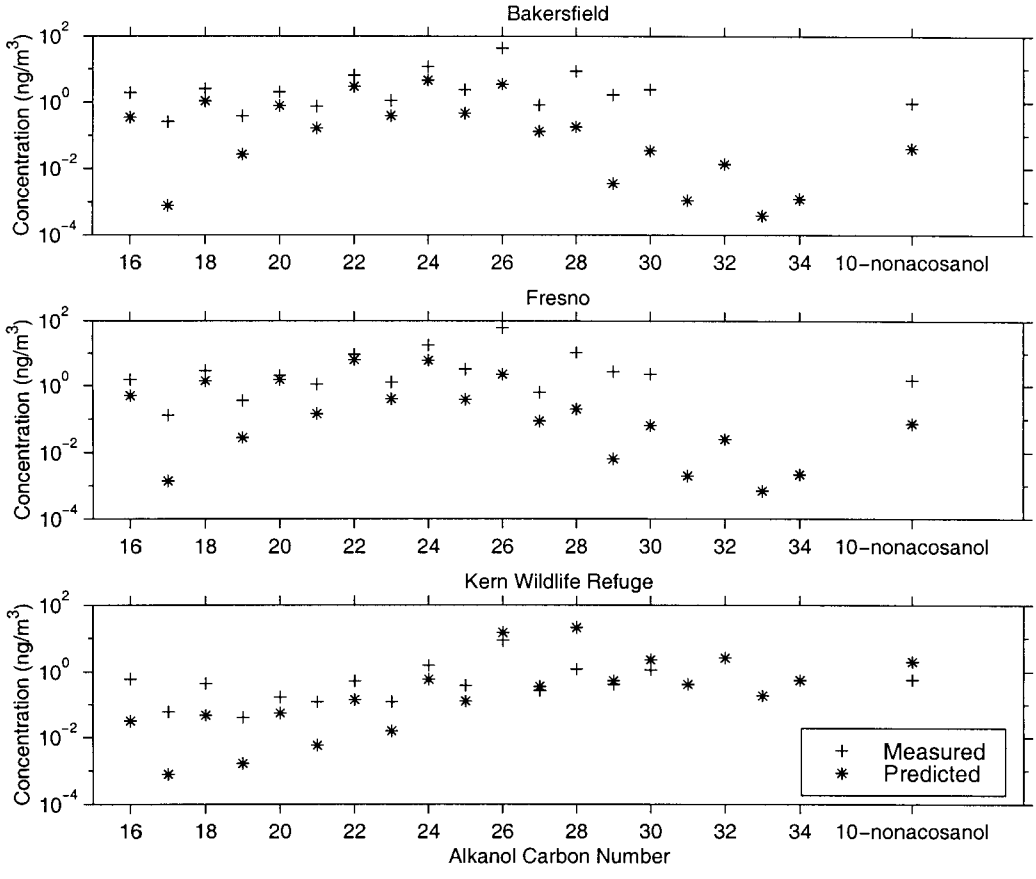

Figure 4.8: Comparison of source-receptor model alkanol concentrations predictions with atmospheric measurements at three sites in the San Joaquin Valley, California.

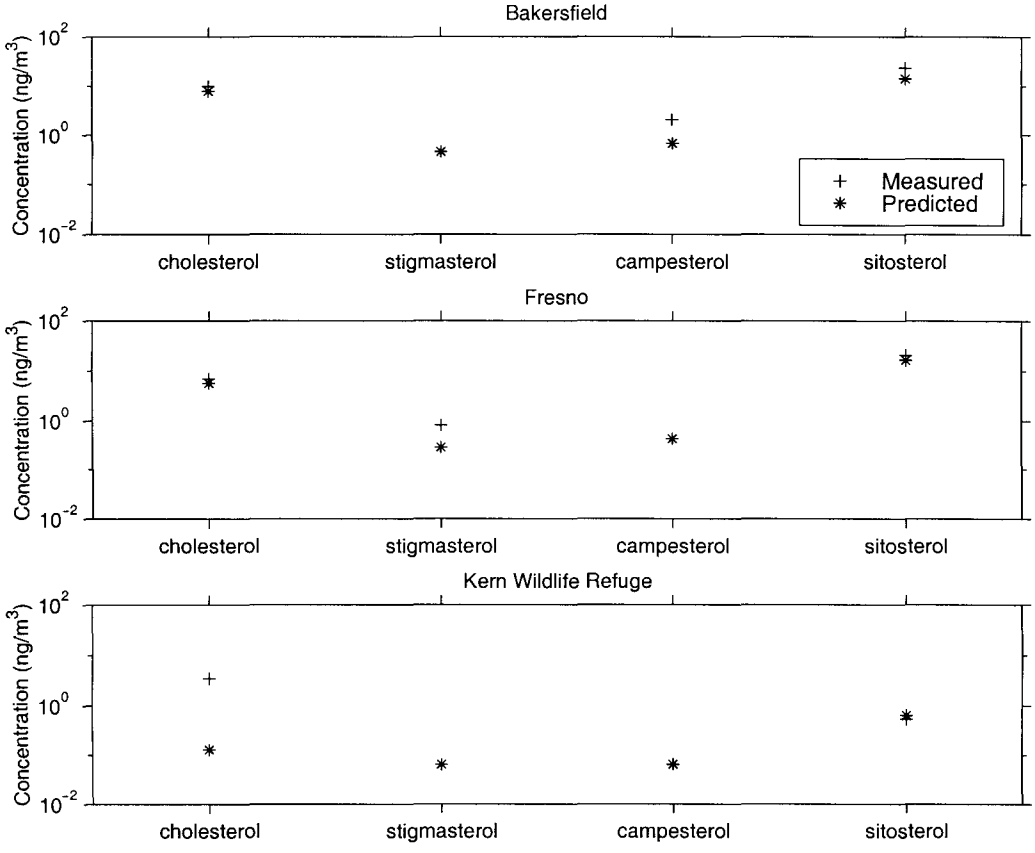

Figure 4.9: Comparison of source-receptor model sterol concentrations predictions with atmospheric measurements at three sites in the San Joaquin Valley, California.

tection limits are higher for higher molecular weight compounds rather than an inaccuracy in the model. The discrepancy between the relative concentrations of C_{26} and C_{28} alkanols in the atmosphere and in the vegetation source sample, however, is significant. It may reflect the fact that the leaf particle sample used in this analysis is a composite of Los Angeles vegetation, which differs from the vegetation that prevails in the San Joaquin Valley, or it may indicate that there is an additional source or sink for these compounds not included in the CMB model.

CMB model predictions are compared with atmospheric sterols concentrations in Figure 4.9. Good agreement is attained between the predictions and observations at the Bakersfield and Fresno sites for cholesterol and β-sitosterol. Stigmasterol and campesterol are at lower concentrations than predicted by the model, but this discrepancy may in part arise from these concentrations being near or below the detection limits. At the Kern Wildlife Refuge site, good agreement is obtained between the predicted and observed concentrations of β-sitosterol, but cholesterol is greatly underpredicted. The CMB model calculations for Kern Wildlife Refuge (see Table 4.10) exclude both meat dust and road dust, two sources of cholesterol. The error incurred in omitting these sources may account for part of the discrepancy between observed and predicted concentrations of cholesterol at the Kern Wildlife Refuge site.

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5 Seasonal and Spatial Characteristics of Formic and Acetic Acids Concentrations in the Southern California Atmosphere

5.1 Introduction

Formic acid (HCOOH) and acetic acid (CH_3COOH) are ubiquitous trace components of the atmosphere. These organic acids have been found to be important contributors to precipitation acidity in nonurban environments (1, 2) including the Venezuelan savanna (3) and the Brazilian central Amazon region (4). Gas phase concentrations ranging from 0.2 to 1 ppb have been reported for many remote areas around the globe (5–12).

Formic and acetic acids concentrations are enhanced in urban areas when compared to remote areas and therefore may play an important role in determining precipitation acidity, the acidity of fog and dew, and the dry deposition flux of acids in urbanized regions. Formate and acetate are found to be major constituents of Los Angeles rainwater (13), and formate is the most abundant anion present, organic or inorganic, in Southern California dew (14). Grosjean (15, 16) shows that daytime summer peak 4-h average gas

Reference: Nolte, C. G.; Solomon, P. A.; Fall, T.; Salmon, L. G.; Cass, G. R. Seasonal and Spatial Characteristics of Formic and Acetic Acids Concentrations in the Southern California Atmosphere. *Environ. Sci. Technol.*, **1997**, 2547–2553.

phase concentrations of formic and acetic acids in Southern California urban air are in the range of 8–10 ppb, higher than the average concentrations of the major inorganic acids, HNO_3 and HCl, during the summer (17, 18).

In addition to being important in the acid deposition budget, exposure to organic acids is known to cause damage to a wide range of materials, including shells, fossils, sandstone, and lead. Organic acid vapors emitted by wooden storage containers in art museums have been observed to corrode objects made of lead or lead-containing alloys such as pewter and bronze (19). Both formic and acetic acids are primary damaging agents, reacting to form a white efflorescence or even a heavy frosting of lead formate or lead acetate crystals, causing permanent pitting and scarring. High concentrations of organic acids in outdoor urban air have the potential to cause similar damage to lead, pewter, and bronze objects, particularly within buildings that have a high air exchange rate with the outdoors.

There are many potential sources of atmospheric formic and acetic acids. However, the relative importance of various pathways that could lead to the introduction of formic and acetic acids into the atmosphere has not yet been identified conclusively. The seasonality in concentrations observed at remote sites (2, 9) is consistent with substantial contributions from vegetative or biogenic emissions, especially during the growing season. Photochemical oxidation of isoprene in particular has been suggested to be an important biogenic source of formic acid (4, 9, 20). Known anthropogenic primary emissions sources include direct emissions from automotive exhaust (21) and combustion of coal, wood, and agricultural waste (9, 12). Acetic acid is reported to be emitted in much greater amounts than formic acid in combustion processes (9). The ozone-olefin reaction has been suggested to yield significant amounts of formic and acetic acids (22, 23), but some studies have found

no evidence that this pathway is an important source (8). Atmospheric gas phase oxidation of formaldehyde by hydroperoxyl radicals also has been suggested as a source of formic acid (24), but this reaction is expected to be too slow at atmospheric concentrations to be the main contributor to atmospheric HCOOH levels (25). Acetic acid can be formed from radical recombination reactions between acetyl peroxy and other peroxy radicals (26–28). Aqueous phase oxidation of formaldehyde by hydroxyl radicals, with subsequent volatilization to the gas phase upon fog or cloud evaporation, also has been proposed as an important pathway for formic acid formation (25, 29).

Because formic and acetic acids have not been regulated as air pollutants, they have not been subject to routine monitoring. With the exception of the 15-month study of Talbot et al. (9) at one remote site in eastern Virginia and a year-long study by Grosjean (30) at Upland, CA, past observations have generally been limited to intensive sampling periods at a single location with a duration of at most a few days. Most of these field studies (e.g., references 4, 10, 12, 15, 31) have focused on determining the diurnal variation of formic and acetic acids concentrations and have usually observed that concentrations peak in the middle of the afternoon and decline at night. Rather little long-term monitoring, however, has been undertaken to define average concentrations plus seasonal and spatial variations, particularly in urban areas. In this paper, experimental data collected at nine monitoring sites throughout the Los Angeles area in 1986 will be reported to document the long-term average concentrations and spatial distribution of formic acid and acetic acid in the Southern California atmosphere. To the author's knowledge, this constitutes the largest database reported for these species. The seasonal and spatial characteristics of these data then will be examined for clues as to the principal sources of formic and acetic acids.

5.2 Experimental Methods

During the calendar year 1986, gas phase acids, ammonia, and atmospheric particulate matter concentrations were measured at nine sampling sites in the Los Angeles area, as depicted in Figure 5.1. All sites except Tanbark Flats and San Nicolas Island were collocated with continuous air monitoring stations operated by the South Coast Air Quality Management District (32, 33). The Tanbark Flats site was located in the San Gabriel Mountains north of San Dimas, in the Angeles National Forest, at an elevation of approximately 870 m. The San Nicolas Island air monitoring site was located at the meteorological station on that island, approximately 140 km southwest of the Los Angeles coastline. This remote, offshore location was chosen to determine background pollutant levels entering the Los Angeles area from the upwind marine environment.

PM_{10} aerosol concentration and chemical composition as well as the concentrations of HNO_3 and HCl measured during these experiments have been described previously (17, 18, 34). Gas phase formic and acetic acids were measured over 24-h averaging times at 6-d intervals at each site using the tandem filter method. Inert polytetrafluoroethylene (PTFE) prefilters were used to remove particulate matter from the airstream prior to collection of gaseous formic and acetic acids on two KOH impregnated 47-mm diameter quartz fiber backup filters in series (Pallflex 2500 QAO). The quartz fiber filters were prebaked for at least 3 h at 750 °C before being spiked with KOH in order to reduce organic contamination. Filters were installed the day prior to and removed the day after sample collection. The nominal air flow rate through the tandem filter pack was 4.9 L min^{-1}, with flow rates monitored before and after sampling by a rotameter that had been factory calibrated

with an accuracy of 1% full scale. Flow rate checks were performed to ensure that the filter holders were not leaking and to verify that filter clogging had not occurred. After sampling, filters were stored in prelabeled Petri dishes at −25 °C until analysis.

Filters were leached by lightly shaking each of them in 10 mL of distilled, deionized water for 3 h. Formic and acetic acids were analyzed as formate and acetate using ion chromatography (Dionex Model 2020i). Concentrations of $HCOO^-$ and CH_3COO^- were determined relative to laboratory standards of known concentration prepared from ACS grade analytical reagents. Instrument detection limits were determined to be 0.9 μg filter^{-1} formate and 2.3 μg filter^{-1} acetate. Field blanks equal in number to 10% of the actual ambient samples were obtained and analyzed in the same manner. Blank values averaged 3.6 ± 1.5 μg filter^{-1} formate and 23 ± 17 μg filter^{-1} acetate. Single sample analytical precision, determined from duplicate (split filters analyzed separately) or replicate (repeat analysis of a filter extract) measurements, was found to be ± 2.8% formate and ± 4.6% acetate. Final error estimates were calculated by the statistical propagation of the sample, filter blank, and sampling volume precisions. The average relative precision (1 σ) was ± 10.4% for formic acid, while the concentration-weighted average precision was ± 6.6%. Due to the higher variability of acetate in the blanks, the acetic acid measurements are less precise; the concentration-weighted average precision was ± 38.0% (typically about ± 1 ppb), with the precision better than ± 20% for peak concentrations greater than about 10 ppb. The uncertainty in the long-term means computed from sample sets collected over many months is of course much smaller.

In the absence of a large database on organic acids concentrations in the Los Angeles atmosphere, the quantity of KOH used to prepare the alkaline-

impregnated filters had to be estimated initially. Analysis of the earliest samples taken showed excessive breakthrough of organic acids onto the second KOH-impregnated backup filter of each set. The quantity of KOH spiked onto each filter was therefore increased to 1 mL of 0.1 *M* KOH in distilled, deionized water, and the subsequent collection of organic acids data proceeded without incident. Accordingly, only data from the final eight months of 1986 are reported here.

Keene et al. (35) reported that alkaline filter techniques for measuring gas phase formic acid may be subject to a significant positive interference from the reaction of aldehydes with the sampling media to generate HCOOH subsequent to collection. When excess formaldehyde was added to the airstream, they detected increased levels of formate on alkaline filters. Other investigators, however (36, 37), have performed similar experiments and concluded that the extent of artifact production of formic acid from formaldehyde is negligible. A different possible artifact that could arise during sampling is the adsorption of gas phase formic or acetic acid onto particulate matter collected on the PTFE prefilter (38). Measurements made during the August 1986 Carbon Species Methods Comparison Study (CSMCS) conducted in Glendora, CA, found that 94% of the total formate measured on PTFE plus KOH filters in a stacked filter unit and 88% of the total measured acetate were detected on the KOH filters (16). Thus, the maximum extent of this negative sampling artifact under conditions found in the South Coast Air Basin is 6% for formic acid and 12% for acetic acid even if all of the particulate formate and acetate are attributed to adsorption of gas phase formic and acetic acids. Furthermore, as part of CSMCS, Grosjean et al. (39) obtained comparable results when using both an alkaline trap-liquid chromatography method and Fourier transform infrared spectroscopy (FTIR) simultaneous to

measure formic acid. Since FTIR is not subject to bias from formaldehyde and uses no PTFE particle prefilter, this provides a degree of confidence in the reliability of sampling formic acid in Southern California with alkaline traps.

The decomposition of peroxyacetyl nitrate (PAN) to form acetate plus nitrite in alkaline media may constitute a source of positive interference in measuring ambient acetic acid. Grosjean and Parmar (36) investigated the extent of this potential artifact by determining the NO_2^-/PAN ratio in daytime summer Southern California air samples, using an alkaline trap to measure the gas phase nitrite concentrations. Assuming that all of the nitrite collected was due to PAN decomposition in the alkaline trap, they derived an estimate of 11–17% as an upper limit for the positive bias due to PAN in measuring gas phase acetic acid. In this work we make no further distinction between acetate derived from true acetic acid and PAN-derived acetate and report all acetate as "acetic acid," recognizing that the values reported constitute an upper bound on the true acetic acid concentration.

For use in the data interpretation that follows, meteorological observations routinely made at local airports, including temperature, dew point, wind speed and direction, and fog observations, were obtained from the National Climatic Data Center. Data from the closest airport or other meteorological observation site were associated with each air monitoring station, as shown in Table 5.1. Since there are virtually no important anthropogenic sources at or upwind of San Nicolas Island, and as the formic and acetic acids concentrations there are very low, there is no reason to process the San Nicolas Island meteorological data during the later analysis of dilution effects on source emissions. For this reason, San Nicolas Island is excluded from Table 5.1. Temperature soundings taken at 0500 hours daily at Loyola

Table 5.1: Air monitoring sites and their associated meteorological observation stations, 1986.

Air Monitoring Site	Associated Meteorological Station
Hawthorne	Los Angeles International Airport
Long Beach	Long Beach Airport
Anaheim	USMC Air Station, Tustin
Downtown Los Angeles	Burbank-Glendale-Pasadena Airport
Burbank	Burbank-Glendale-Pasadena Airport
Tanbark Flats	Tanbark Flats USFS Station
Upland	Ontario Airport
Rubidoux	March Air Force Base, Riverside

Marymount University near Hawthorne were provided by the South Coast Air Quality Management District and were used to determine the morning mixing depth over the west Los Angeles coastal area. Incident solar radiation measurements were made at Riverside, CA, by the California Irrigation Management Information System.

5.3 Results and Discussion

5.3.1 Ambient Levels of Formic and Acetic Acids in Southern California

The arithmetic means of the 24-h average formic and acetic acids concentrations over the period May–December 1986 are shown in Figure 5.1. As a general trend, it can be seen that concentrations are lowest over the ocean at San Nicolas Island, averaging 1.4 ppb for formic acid and 0.6 ppb for acetic acid. HCOOH and CH_3COOH concentrations rise to approximately 3 ppb each at the near coastal sites at Hawthorne and Long Beach. Average formic and acetic acids concentrations increase to approximately 5 ppb HCOOH and 4 ppb CH_3COOH at areas of high traffic density (Burbank and Down-

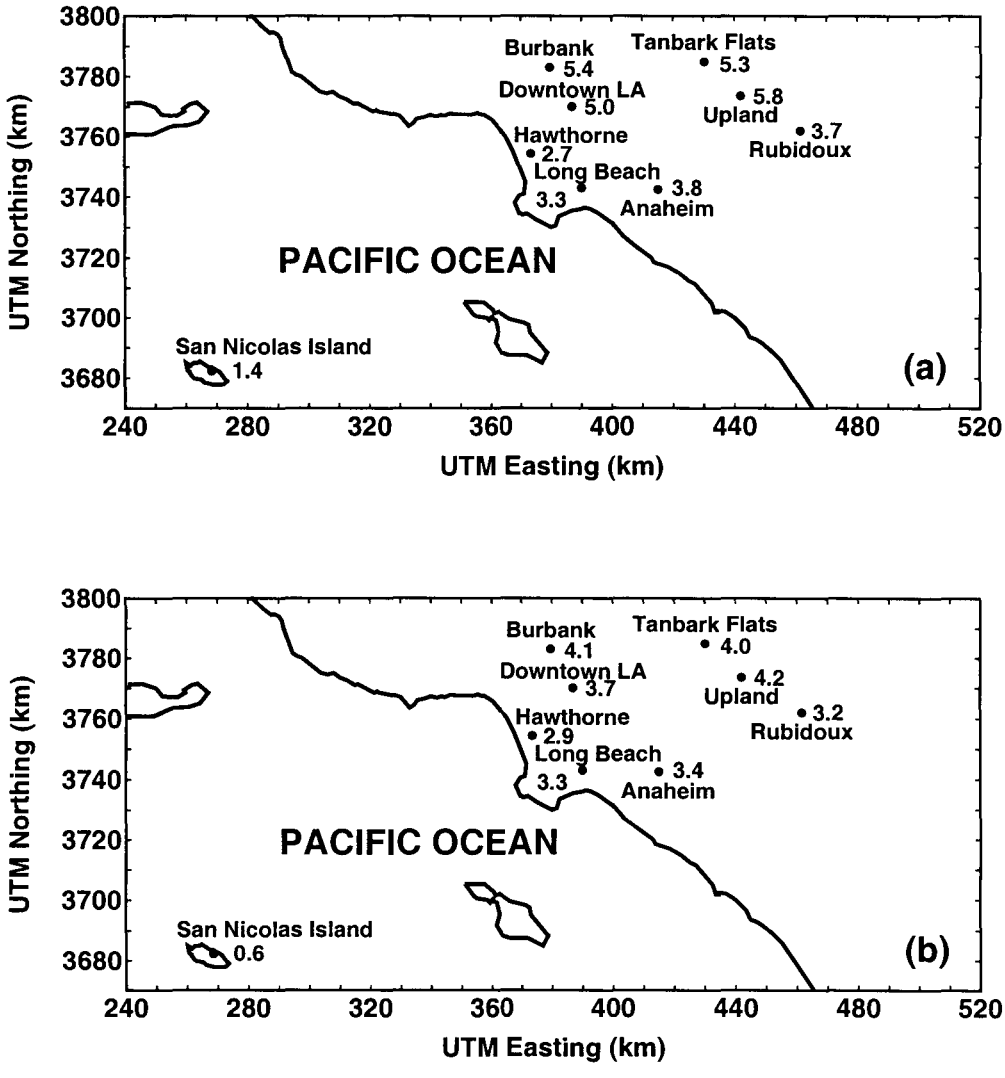

Figure 5.1: Southern California air monitoring network. Arithmetic mean 24-h average (a) formic acid and (b) acetic acid concentrations over the period May–December 1986 are given in ppb, assuming standard conditions of 25 °C and 1 atm pressure. The uncertainty in the mean concentrations over the days observed due to the experimental precision is ≤ 0.05 ppb for formic acid and ≤ 0.4 ppb for acetic acid at all sites.

town Los Angeles), and remain at about the same level at the downwind locations at Upland and Tanbark Flats. Rubidoux is generally downwind of Anaheim in the summer (40); average formic acid and acetic acid concentrations are approximately the same at these two sites (3.7–3.8 ppb formic acid and 3.2–3.4 ppb acetic acid). Peak 24-h average formic and acetic acids concentrations are typically 2–3 times greater than the 8-month average concentrations for the same site, as shown in Figure 5.2. The highest peaks occur at the downwind locations at Upland and Tanbark Flats. Peak 24-h average formic and acetic acids concentrations for the year at each monitoring site generally occur on days with higher than average concentrations throughout the air basin, though peak concentrations do not all occur on the same day of the year at all sites.

Formic and acetic acids time series plots for each of the nine sites are presented in Figure 5.3. It can be seen that fluctuations in formic acid and acetic acid concentrations are highly correlated, and that these two gas phase organic acids are present in approximately equal concentrations at the same sites on most days. No seasonal variation is evident for the coastal sites. Burbank and the three inland sites, Tanbark Flats, Upland, and Rubidoux, show a marked increase in organic acid levels during the summer months. The data at San Nicolas Island show that background concentrations of formic and acetic acids in marine air upwind of the city are low and nearly uniform. The higher but fairly constant levels of formic and acetic acids at the near coastal sites at Long Beach and Hawthorne suggest a relatively constant addition of these acids from primary emissions sources. The still higher and more variable concentrations at inland sites suggest that the marine background and primary source emissions are supplemented by episodic photochemical or aqueous phase chemical production during transport to the downwind sites

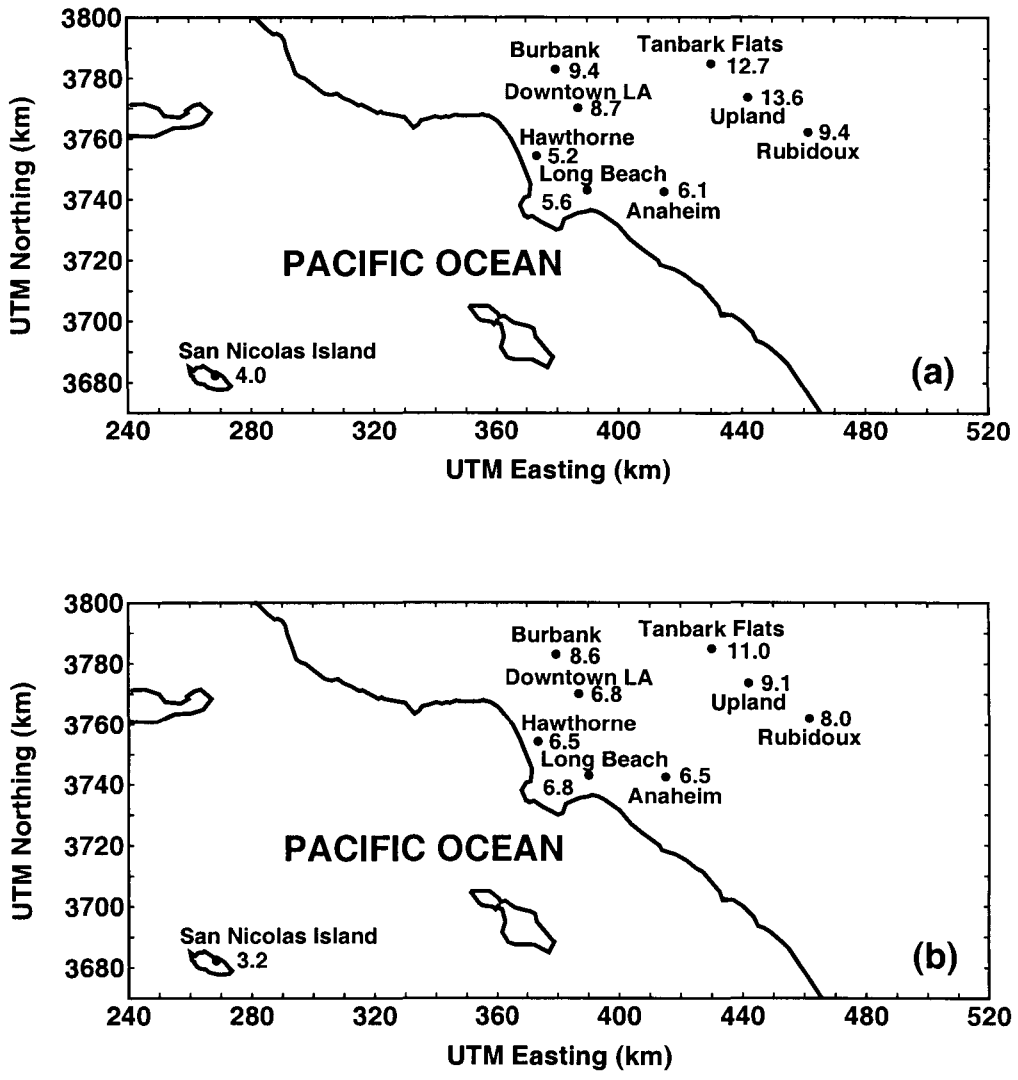

Figure 5.2: Peak 24-h average organic acids concentrations over the period May–December 1986, in ppb: (a) formic acid and (b) acetic acid.

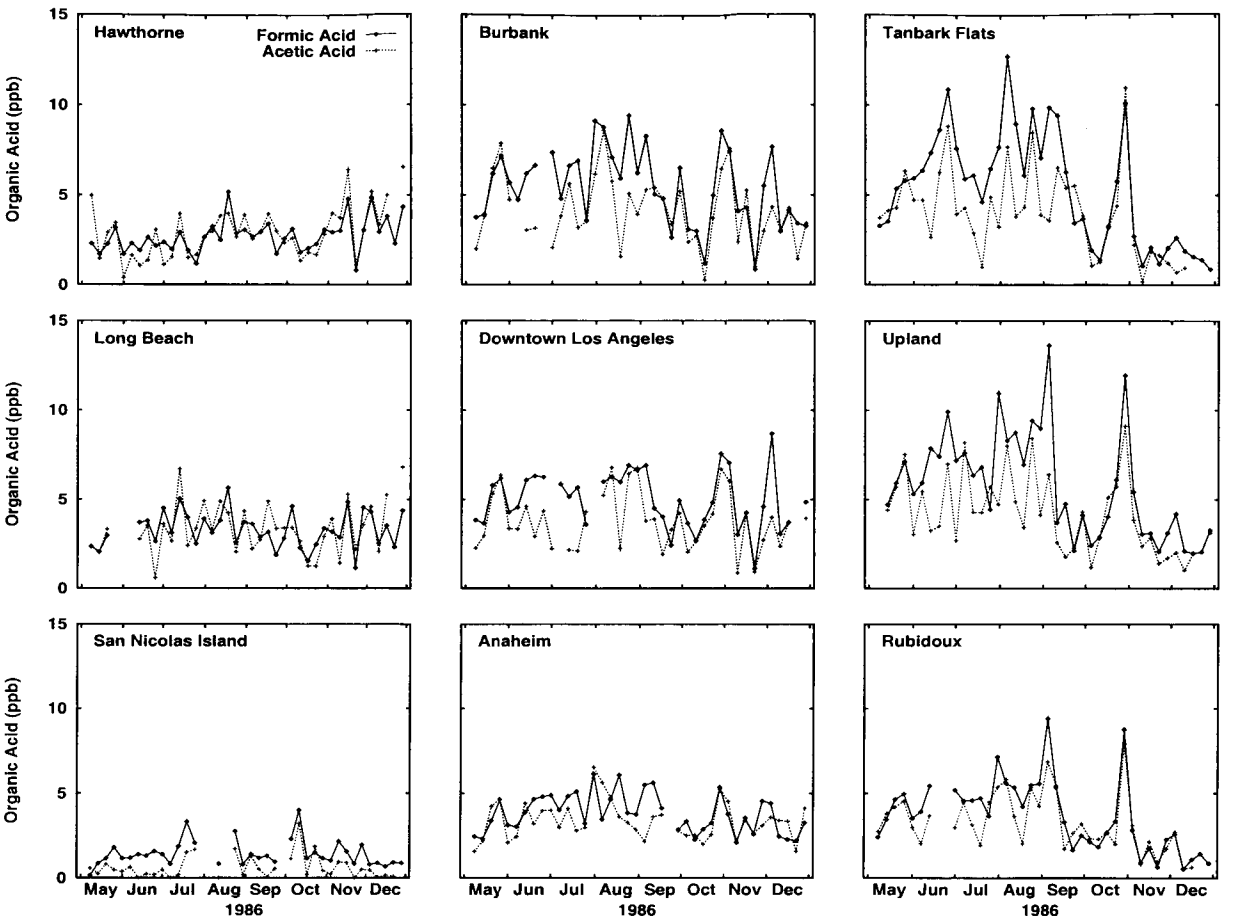

Figure 5.3: Time series of formic and acetic acids concentrations in Southern California. Data points represent 24-h averages. Line breaks indicate missing data.

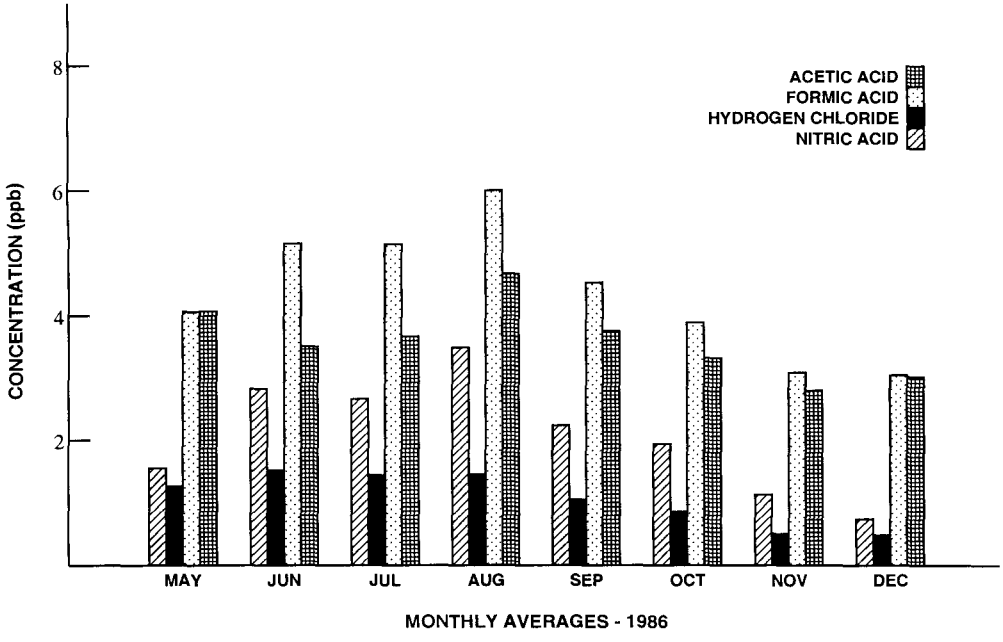

Figure 5.4: Concentrations of gas phase acids in the Los Angeles air basin in 1986, averaged over the eight on-land air monitoring sites shown in Figure 5.1. HNO_3 data adapted from Solomon et al. (17); HCl data adapted from Eldering et al. (18).

in the summer and sometimes the fall seasons.

Concentrations of formic and acetic acids averaged over eight sites in the Los Angeles basin (excluding San Nicolas Island) are shown in Figure 5.4 along with basinwide monthly average concentrations of HCl and HNO_3, the major inorganic acids species measured in this study (17, 18). The average concentration of acetic acid in the Los Angeles basin exhibits little seasonal variation, but average formic acid concentrations peak during the summer months. These average urban formic and acetic acids concentrations are substantially higher than annual average HNO_3 concentrations (urban annual

mean 1.2–2.7 ppb) and HCl concentrations (urban annual mean 0.53–1.25 ppb). Previous observations that formic acid and acetic acid are the most abundant acids present in the atmosphere (15, 16) and in dew (14) in Southern California in the summer thus apply in general over the rest of the year and over each of the large number of urban monitoring sites studied here.

5.3.2 Comparison With Results of Other Studies

It is important to bear in mind that the results from the present work provide 24-h and longer average values, and as such the peak values from the present study should be lower than peak values seen in those other studies which reported midday 4-h averages. Summertime 24-h average concentrations at the downwind receptor sites at Upland and Tanbark Flats during the present study ranged from 4–14 ppb for formic acid and 1–11 ppb for acetic acid. Short-term ($\leq$ 5 min) average formic acid concentrations of up to 19 ppb have been measured by FTIR during summer smog episodes in Pasadena (41), Riverside (42), and Claremont, CA (43), which are all located within our study area. Using an alkaline trap-ion chromatography method nearly identical to that described here, except over a 4-h time scale, Grosjean (15) reported 1.9–10.5 ppb formic acid and 2.5–9.5 ppb acetic acid over a 9-d period during the summer 1985 Nitrogen Species Methods Comparison Study (NSMCS) at Claremont. As part of the 1987 Southern California Air Quality Study (SCAQS), 4-h average formic and acetic acids concentrations were measured at two sites during four 2–3 day periods in the summer and at one site during two 3-d periods in the fall (44). Peak 4-h average concentrations were 20 ppb formic acid during the summer at Claremont and 18 ppb acetic acid during the fall at Long Beach. Formic and acetic acids were measured over five 2–4 day periods at four sites in the western Sierra Nevada mountains,

CA (45). Mean daytime (10-h average) formic acid concentrations were 18 ppb at Tehachapi and 12–13 ppb at three other sites, with peak 10-h averages as high as 40 ppb. Acetic acid concentrations ranged from 0.5–13 ppb. These results at Tehachapi are higher than those obtained in the present study at Tanbark Flats. In a year-long study conducted at a single site at Upland, CA, in 1988–89 (30), the peak 24-h average formic acid concentration observed was 8 ppb, while the annual average concentration was 2.8 ppb, somewhat lower than the results reported here for that site.

Only limited organic acid data are available for urban areas outside Southern California. During a single 10-h daylight period in August, Schultz Tokos et al. (31) observed formic and acetic acids concentrations ranging from 3.1–12.5 ppb and 1.8–7.3 ppb, respectively, over 30-min averaging times in the urban atmosphere of Yokohama, Japan. Six-hour average formic and acetic acids concentrations ranged from 1.8–14.8 ppb and 0.8–5.4 ppb, respectively, during a two-month period in Boston (46). As can be seen from these results, the formic and acetic acids concentrations data presented here for Los Angeles in 1986 is in the range of that measured at other locations or in the same location at other time periods.

5.3.3 Examination of Sources and Production Pathways for Organic Acids

Several possible sources and production mechanisms have been proposed for formic and acetic acids. These include their direct emission into the atmosphere, either from biogenic sources (2, 4) or via anthropogenic activities (4, 12, 21), and atmospheric gas or aqueous phase oxidation of precursor organic compounds (8, 12, 20, 22–29, 45). While a mechanistic air quality model might be envisioned that would explain the cause and effect relation-

ships between pollutant emissions and formic and acetic acids concentrations, such a model is presently beyond the state of the art. As noted in the review by Chebbi and Carlier (47), the emissions fluxes of carboxylic acids from vegetation and soils, the precise mechanism of all important gas phase reactions, as well as the importance of heterogeneous reactions on aerosol particles and on other surfaces in the environment is not fully understood at present. Therefore, at this time the highest use of the present data is to search for clues as to the possible sources and formation pathways for formic and acetic acids through analysis of the meteorological and co-pollutant data from the present experiment to determine whether or not fluctuations in formic or acetic acids concentrations track conditions which are indicative of a particular hypothetical source of organic acids. We adopt this approach to examine the following possible sources of organic acids: direct emissions from widespread area sources (e.g., motor vehicle exhaust; decay of biological material in soils); gas phase photochemical production; and aqueous phase oxidation to form organic acids within fog, clouds, or dew.

We first examine the hypothesis that formic and acetic acids are predominantly primary pollutants, i.e., that they are directly emitted from widespread area sources. Changes in carbon monoxide (CO) or elemental carbon (EC) concentrations from day to day are often used as indicators of the changes in dilution that influence the atmospheric concentrations of directly emitted air pollutants, since CO and EC are not formed photochemically but instead are directly emitted by combustion sources. In the Los Angeles area, both CO and EC are emitted largely from motor vehicle traffic, and daily average traffic volumes are thought to be roughly the same from day to day over the course of the year. In the present study, PM_{10} elemental carbon concentrations, EC, will be used as a surrogate tracer for the

dilution of direct emissions. The EC measurements used were taken on the same days at the same locations and with the same averaging times as the organic acids data, and have been reported previously by Solomon et al. (34). We note that at all sites where CO data are available from South Coast Air Quality Management District air monitoring instruments (i.e., all except San Nicolas Island and Tanbark Flats) our EC values and the reported daily 1-hr average CO peaks are highly correlated. Correlation coefficients range from 0.79–0.94, and all have a p-value ≤ 0.01 (Table 5.2).

Assuming that emissions patterns are similar from day to day, variations in ambient EC concentrations should track changes in the dilution volume of the air basin. Two factors closely related to the dilution volume for inert species such as EC are the scalar average wind speed, WS, and the mixing height, MH, determined from the morning temperature sounding. We define the dilution parameter D as the reciprocal of the product of the scalar average wind speed and the mixing height, $D = \frac{1}{MH}$. Defined in this manner, D is inversely proportional to the effective air volume of the airshed on a given day. Table 5.2 lists correlation coefficients between EC and D. When changes in EC concentrations are examined as an indicator of the degree of dilution of direct emissions, it is found that EC concentrations track the dilution parameter most closely at coastal sites near the location of the lowest morning mixing depths and near where the mixing depth is measured at the coast. If we seek a signal that captures the effect of direct emissions from vehicles and other primary sources on formic and acetic acids concentrations, it is most likely to be detected at the coastal sites.

We now turn to formic and acetic acids, and ask the question of whether or not fluctuations in their concentrations track changes in EC or changes in the dilution parameter. Correlation coefficients of formic and acetic acids

Table 5.2: Pearson correlation coefficients between EC, CO, formic acid, acetic acid, and the dilution parameter D.

Site	EC/CO[a]	EC/D	EC/FA	EC/AA	FA/D	AA/D
Hawthorne	0.91[c]	0.82[c]	0.60[c]	0.61[c]	0.62[c]	0.52[c]
Long Beach	0.88[c]	0.85[c]	0.17	0.21	0.24	0.35[b]
Anaheim	0.85[c]	0.74[c]	0.00	0.10	−0.22	−0.09
Downtown LA	0.94[c]	0.64[c]	0.28	0.02	−0.16	−0.19
Burbank	0.94[c]	0.63[c]	0.16	0.03	−0.21	−0.20
Tanbark Flats	n/a	−0.12	0.74[c]	0.52[c]	−0.41[b]	−0.21
Upland	0.79[c]	0.23	0.52[c]	0.30	−0.49[c]	−0.49[c]
Rubidoux	0.84[c]	0.44[c]	0.34[c]	0.32	−0.37[b]	−0.26

[a]EC, elemental carbon; CO, carbon monoxide; WS, scalar average wind speed; MH, mixing height; $D = \frac{1}{WS \times MH}$; FA, formic acid; AA, acetic acid; n/a, not available.

[b]$p = 0.05$.

[c]$p = 0.01$.

versus EC and D are listed in Table 5.2. These correlation coefficients are highest at Hawthorne near the coast and suggest that much of the formic and acetic acids concentrations at that site could be attributable to local primary emissions sources. At Long Beach, a weaker but consistently positive correlation between the organic acids concentrations and dilution variables also is seen. The small or negative correlations between the dilution variable and organic acids concentrations at the inland sites indicate that processes other than dilution of primary emissions are important in controlling organic acids levels at the other sites. Tanbark Flats is located in the mountains in an area with no local motor vehicle traffic. All pollutants reaching Tanbark Flats are transported to that site from upwind. The positive correlations between EC and formic and acetic acids at that site indicates that all three pollutants arrive together at Tanbark Flats whenever heavily contaminated air is advected over the site. The negative correlations between pollutant concentrations and the dilution volume parameter indicates that transport

Table 5.3: Pearson correlation coefficients with O_3.

Site	T_{avg}[a]	SR	EC	FA	AA
Hawthorne	0.47[c]	0.44[b]	−0.31[b]	0.34[b]	0.15
Long Beach	0.69[c]	0.58[c]	−0.42[c]	0.50[c]	0.14
Anaheim	0.59[c]	0.45[c]	−0.27	0.59[c]	0.19
Downtown LA	0.85[c]	0.68[c]	−0.36[b]	0.51[c]	0.27
Burbank	0.77[c]	0.68[c]	−0.33[b]	0.78[c]	0.47[c]
Upland	0.77[c]	0.66[c]	0.35[b]	0.87[c]	0.61[c]
Rubidoux	0.77[c]	0.65[c]	0.15	0.86[c]	0.61[c]

[a] T_{avg}, daily average temperature; SR, incident solar radiation; EC, elemental carbon; FA, formic acid; AA, acetic acid.
[b] $p = 0.05$
[c] $p = 0.01$

direction matters more than degree of dilution at Tanbark Flats. Upland, which is located not far from Tanbark Flats, seems to share some of these characteristics.

Next, we consider the hypothesis that formic and acetic acids are formed photochemically. Daily peak 1-h average ozone (O_3) concentration measurements made by the South Coast Air Quality Management District at seven of our sites were acquired from the California Air Resources Board (48). We use high ozone concentrations as a marker for days with high rates of gas phase photochemistry. Correlation coefficients between the 24-h average temperature, incident solar radiation, EC, formic and acetic acids and ozone are listed in Table 5.3. It is evident that high O_3 concentration peaks are positively correlated with days having high temperature and high solar radiation, as expected. In the western part of the air basin, factors that produce high EC concentrations (e.g., winter air stagnation events) occur at a different time of year than high photochemical smog events, hence the negative correlations between high ozone events and high elemental carbon concentration

events. At Upland and Rubidoux at the eastern end of the air basin, EC levels are higher on days with high O_3. This is due to the transport of material emitted within the Los Angeles urban core to downwind locations on high photochemical smog days, rather than to dominance by local sources of EC emitted in the vicinity of Upland or Rubidoux. Most importantly, we note that there is a progressively improving correlation between formic and acetic acids and O_3 as air parcels move inland toward the downwind photochemical smog receptor sites. These results suggest that for the eastern portion of the air basin, photochemical production during transport dominates local primary emissions of formic and acetic acids.

Finally, we consider evidence that could support or refute the hypothesis that formic and acetic acids are formed by aqueous phase oxidation within liquid fog droplets. Since it is known that in the Los Angeles basin high sulfate levels are formed primarily within liquid droplets in the presence of high relative humidity and fog (49–51), we use particulate sulfate, SO_4^{2-}, as our primary marker for the occurrence of fog processing. In addition, the average relative humidity, RH, and the number of hours that fog was observed during the day, NFOG, can be used to characterize the potential for aqueous phase transformations. However, it must be noted that if NFOG is computed only from fog observations at airports located near the air monitoring sites where the formic and acetic acids measurements were made, then those local fog observations may not capture a Lagrangian description of the conditions experienced by air parcels as they are advected across the air basin to the sampling sites. An air monitoring site at which fog was not observed during a day may sample air parcels that encountered a fog upwind near the coast earlier in the day. Accordingly, for the inland sites (i.e., all except Hawthorne and Long Beach), NFOG was determined by counting the

Table 5.4: Pearson correlation coefficients with SO_4^{2-}.

Site	RH[a]	NFOG	O_3	FA	AA
Hawthorne	0.63[c]	0.66[c]	0.30	0.02	−0.09
Long Beach	0.45[c]	0.63[c]	0.40[b]	0.10	−0.05
Anaheim	0.43[c]	0.68[c]	0.47[c]	0.57[c]	0.54[c]
Downtown LA	0.74[c]	0.69[c]	0.44[c]	0.42[c]	0.62[c]
Burbank	0.76[c]	0.73[c]	0.56[c]	0.50[c]	0.58[c]
Tanbark Flats	0.57[c]	0.56[c]	n/a	0.69[c]	0.64[c]
Upland	0.61[c]	0.67[c]	0.64[c]	0.72[c]	0.68[c]
Rubidoux	0.46[c]	0.61[c]	0.69[c]	0.83[c]	0.79[c]

[a]RH, average relative humidity; NFOG, number of hours per day fog was observed; FA, formic acid; AA, acetic acid.
[b]p = 0.05
[c]p = 0.01

number of hours in each day that fog was observed at some point in the Los Angeles basin. Since fog downwind of the coastal sites at Hawthorne and Long Beach does not affect pollutant levels at the coast, the NFOG parameter values for Hawthorne and Long Beach were based only on data from the local meteorological observation station representing those areas (Table 5.1).

The correlation coefficients of RH, NFOG, peak O_3, and formic and acetic acids with SO_4^{2-} are presented in Table 5.4. Sulfate concentrations are positively correlated with both aqueous phase indicators at all sites. Formic and acetic acids concentrations at inland sites are highly correlated with sulfate concentrations, while at the coastal sites, Hawthorne and Long Beach, the same relationship to sulfate concentrations does not exist. This suggests that different processes are important in determining formic and acetic acids and sulfate concentrations at the coast, but that similar processes control their concentrations inland. This is consistent with the hypothesis that direct emissions sources plus marine background concentrations dominate formic

and acetic acid concentrations at Hawthorne and Long Beach, but that atmospheric conversion processes are important at locations downwind.

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6 Gas Phase C_2–C_{10} Organic Acids Concentrations in the Los Angeles Atmosphere

6.1 Introduction

Much of the research on atmospheric carboxylic acids has focused on formic and acetic acids, both in remote environments (1–4) and in urban areas (5–10). Formate and acetate are found to be major constituents of rain (11, 12) and dew (13) in Los Angeles. Formic and acetic acids have been measured in automotive emissions (3, 14) and in the smoke from biomass combustion (3). Higher molecular weight acids also are reported in motor vehicle exhaust (14, 15). Several chemical reaction mechanisms have been proposed for the formation of organic acids in the atmosphere. These include the reaction of ozone with olefinic hydrocarbons (16, 17), particularly isoprene (3, 18, 19), aldehyde oxidation by hydroxyl radicals (20, 21), and radical recombination reactions between acetyl peroxy and other peroxy radicals (22). Little is known, however, about the relative importance of these various chemical reaction mechanisms versus direct emissions from anthropogenic and biogenic sources.

Substantial attention has been given to measurements of the atmospheric concentrations of particle phase carboxylic acids, including aliphatic dicarboxylic acids (12, 23–26), higher molecular weight alkanoic acids (26, 27),

Reference: Nolte, C. G.; Fraser, M. P.; Cass, G. R. Gas Phase C_2–C_{10} Organic Acids Concentrations in the Los Angeles Atmosphere. *Environ. Sci. Technol.*, **1999**, 540–545.

and aromatic polycarboxylic acids (26, 27). This work instead focuses on gas phase carboxylic acids > C_2. Due to the analytic difficulty in quantifying trace levels of volatile polar compounds, relatively few measurements of the ambient concentrations of these species have been reported. One approach to making such measurements is to use a free fatty acid phase (FFAP) gas chromatographic (GC) column to effect the separation of the homologous series of the alkanoic acids. Hoshika (28) used such a technique to determine the gas phase concentrations of C_2–C_5 alkanoic acids in ambient urban air and in air near a poultry manure pen. Various derivatization techniques also have been employed to make the organic acids less polar and thus amenable to analysis using standard GC columns. Kawamura et al. (14) used such a derivatization technique to measure gas phase C_1–C_{10} monocarboxylic acids plus benzoic acid in atmospheric samples taken in 1984 at a single site in West Los Angeles. To the author's knowledge, comprehensive measurements of the gas phase concentrations of organic acids > C_2 have never been made over a network of air monitoring stations during an extended urban smog episode.

The present study reports the gas phase concentrations of C_2–C_{10} monocarboxylic acids and benzoic acid during a severe photochemical smog event in the Los Angeles area during which peak ozone concentrations reached 0.3 ppm. These data have been collected as part of a larger study of vapor phase, semivolatile, and particle phase organic compounds (29).

6.2 Experimental Methods

6.2.1 Sample Collection

During the summer of 1993, a field experiment was conducted to measure simultaneously the concentrations of as many individual vapor phase,

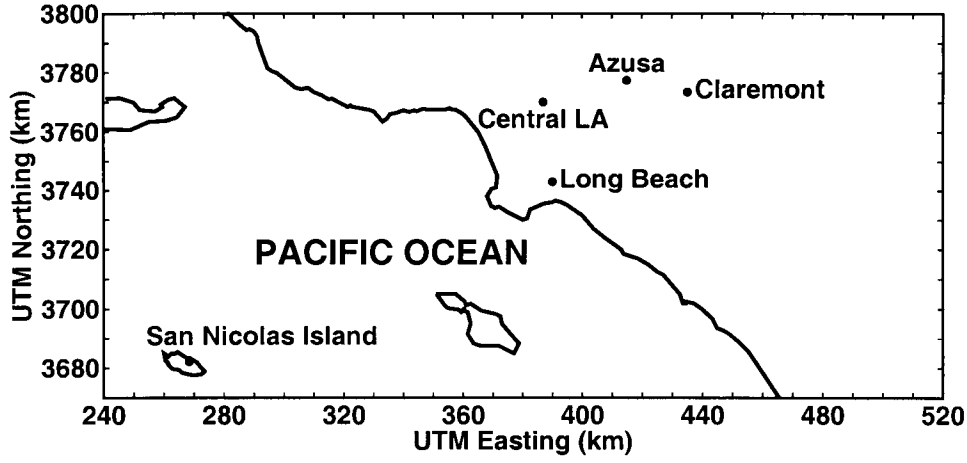

Figure 6.1: Map of Southern California showing the locations of the air monitoring stations used.

semivolatile, and particle phase organic compounds as possible (29). The purpose of the experiment was to acquire a comprehensive data set for the evaluation of air quality models that predict the concentrations of individual organic species in the atmosphere. Samples were collected at five sites in Southern California during a 2-day photochemical smog episode on September 8–9, 1993. The sampling locations used in the study are shown in the map of Figure 6.1. Samples of 4 h duration centered within consecutive 6-h periods were collected at four sites in the Los Angeles basin (Long Beach, Central Los Angeles, Azusa, and Claremont). Samples of somewhat longer duration (8–11 h) were collected at San Nicolas Island, a remote offshore site intended to characterize clean background conditions prevailing upwind of the city. The severity of the photochemical smog episode and the overall experimental design are more fully described by Fraser et al. (29).

Organic acids were collected by two separate sampling methods: a high-

volume dichotomous sampler that used quartz fiber filters followed by polyurethane foam (PUF) cartridges, plus a low-volume particulate matter sampler in which two potassium hydroxide (KOH) impregnated 47-mm diameter quartz fiber filters were placed in series downstream of a Teflon particle prefilter. Particle phase and high molecular weight vapor phase organic acids were collected with the high-volume dichotomous sampler filters and PUF cartridges, respectively, while the KOH impregnated filters deployed with the low-volume (10 L min^{-1}) sampler were used to measure the low molecular weight vapor phase acids, which are present at much higher concentrations. The KOH impregnated filters have a lower *n*-alkanoic acids blank value than is the case for the PUF material. The high-volume quartz fiber filter and PUF samples are discussed elsewhere (26, 30); only the low molecular weight gas phase acids collected on the KOH impregnated filters are reported here. The quartz fiber filters were prebaked at 550 °C for at least 8 h in order to reduce organic contamination and were then spiked with 1.0 mL of 0.1 M KOH solution. Filters were stored and transported in individual Petri dishes lined with annealed aluminum foil and sealed with Teflon tape. At the end of each sampling period, filters were promptly removed from the samplers and refrigerated until being returned to the laboratory, where they were placed in freezers at −21 °C until analysis.

The decomposition of peroxyacetyl nitrate (PAN) to form acetate plus nitrite in alkaline media may constitute a source of positive interference in measuring ambient acetic acid. Grosjean and Parmar (31) investigated the extent of this potential artifact by determining the NO_2^-/PAN ratio in daytime summer Southern California ambient air samples, using an alkaline trap to measure the gas phase nitrite concentrations. Assuming that all of the nitrite collected was due to PAN decomposition in the alkaline trap, they

derived an estimate of 11–17% as an upper limit for the positive bias due to PAN in measuring acetic acid. PAN and peroxypropionyl nitrate (PPN) were measured as part of the present field experiment. During this study period, 48-h average PAN concentrations ranged from 1.35–3.76 ppb between the four urban monitoring sites, while PPN ranged from 0.28–0.58 ppb (32).

6.2.2 Analytical Methods

Prior to extraction, each sample was spiked with a constant amount of a recovery standard containing deuterated propionic, hexanoic, and benzoic acids. The quantity of the spike used was chosen to be comparable to the concentrations of the actual organic acids that were expected to be present in a typical atmospheric sample. The two KOH filters from each sample were extracted together three times by mild sonication in 5 mL of HPLC grade water for 10 min. Organic acids concentrations were determined by the method first used by Kawamura and Kaplan (11, 14) that will be described briefly here. The extracts were combined and passed through a polypropylene column packed with a cation exchange resin (Bio-Rad Poly-Prep, AG 50W-X8 resin, 100–200 mesh, K^+ form). The solution pH was adjusted to 8.0–9.0 with 1 M HCl, and the solution was dried in a rotary evaporator. Potassium carboxylates ($RCOO^-K^+$) were dissolved in 5 mL of acetonitrile and converted to bromophenacyl esters by addition of 2,4′-dibromoacetophenone (reagent, 40 μL of 0.2 M solution in CH_2Cl_2) and dicyclohexano-18-crown-6 (catalyst, 25 μL of 0.03 M solution in acetonitrile) and heating in a water bath at 80 °C for 1 h. Following derivatization, the solution was again dried in a rotary evaporator and redissolved in a 2:1 mixture of hexane/CH_2Cl_2. The samples were concentrated to a final volume of 100–250 μL under nitrogen before analysis by gas chromatography/mass spectrometry (GC/MS).

Samples were analyzed with a Hewlett-Packard GC/MS system (GC Model 5890; MSD Model 5972) using a 30 m DB-5MS column (0.25 mm ID, 0.25 μm film thickness; J&W Scientific). The gas chromatographic conditions used were as follows: (1) splitless injection of 1 μL sample at 200 °C; (2) constant He carrier gas flow rate of 1.0 mL min^{-1}; (3) GC oven temperature hold at 40 °C for 6 min; (4) oven temperature ramp at 30 °C min^{-1} to 160 °C; (5) temperature ramp at 8 °C min^{-1} to 290 °C; and (6) isothermal hold at 290 °C for 3 min. The mass spectrometer scanned from 45 to 400 Da twice per second. 1-Phenyldodecane was used as a coinjection standard to monitor the response of the instrument. An authentic standard containing each of the compounds studied here as well as the alkenoic acids acrylic acid and crotonic acid was spiked onto KOH filters and derivatized in the same manner as described above for the atmospheric samples, ensuring accurate peak identification and compound response factors. Peaks in the single ion GC/MS traces were integrated for each of the compounds of interest. The amounts of acids in the samples were quantified relative to the known amounts of deuterated acids spiked onto the filters before extraction. The recovery of the compounds in the deuterated spike was found to be reasonably uniform across all of the samples.

6.2.3 Calibration and Detection Limits

The authentic standard suite was analyzed nine times at concentrations spanning two orders of magnitude (ca. 1–100 ng injected), bracketing the range of concentrations observed in the atmospheric samples. A constant amount of the deuterated acids internal standard was spiked onto all samples. For all compounds studied here, the instrumental response (peak area relative to deuterated acid peak area) was linearly related to the compound mass spiked

onto the filter. Relative response factors calculated from these standard runs were determined with a precision of 10–20%.

Procedural blanks were analyzed by the same extraction and quantification methods described above. The recovery of formic acid was found to be highly variable. Accordingly, formic acid concentrations were not quantified. The alkenoic acids acrylic acid and crotonic acid were not found in any of the atmospheric samples. It is possible, however, that acrylic and crotonic acids may have been present in the atmosphere but reacted with ozone while trapped on the alkaline filter. Acids on the blank filters mainly consisted of minor amounts of acetic acid and were generally low compared to values in the urban atmospheric samples. Atmospheric concentration data presented below have been corrected by subtraction of the values observed in the blanks. Error bounds were determined from statistical propagation of analytic uncertainties and the variability of the blanks.

6.3 Results and Discussion

6.3.1 Atmospheric Samples

Average gas phase carboxylic acids concentrations at each air monitoring site over the 2-day episode are presented in Table 1. Acetic acid concentrations at the remote offshore site at San Nicolas Island are low compared to concentrations seen at the urban sites but are still significantly above the filter blank values. Propionic acid concentrations in the San Nicolas Island samples are only slightly greater than the blank values, while the levels of the other acids $> C_3$ are virtually indistinguishable from the blanks. All of the acids studied here are detected at much higher concentrations in the urban atmospheric samples than at San Nicolas Island, with generally progressively increasing concentrations as air masses are advected from the coast (e.g., Long Beach)

to Central Los Angeles and Azusa. This indicates that these acid species arise from either direct emissions from local primary sources in the urban area or are formed in the atmosphere by chemical reaction of locally emitted precursor volatile organic compounds (VOC). The diurnal variation of the acids concentrations is examined below in an attempt to assess the relative importance of direct emissions versus atmospheric formation.

Acetic acid is by far the most abundant carboxylic acid species studied at all sites, with average concentrations ranging from 1.8 μg m^{-3} (0.7 ppb) at San Nicolas Island to 19.8 μg m^{-3} (8.1 ppb) at Azusa. These concentrations are in the range of those previously reported for the Southern California atmosphere (5, 6, 33–35). Propionic acid is the next most abundant species, with generally lesser quantities of acids as carbon chain length is increased. Included for comparison in Table 1 are compound concentrations measured by the same technique at a single location in West Los Angeles in 1984 (14). The atmospheric concentrations observed during the severe photochemical smog episode studied here are approximately 2–7 times higher than those reported earlier at West Los Angeles in the 1980s, though the relative distribution of the various acid species is similar. We note that the concentrations of C_4–C_9 *n*-alkanoic acids in the gas phase are much greater than the concentrations of the C_8–C_{24} *n*-alkanoic acids in the particle phase reported by Fraser et al. (26, 30). Simultaneous measurements reported by Fraser et al. using PUF cartridges (26, 30) show close agreement for benzoic acid, the only gas phase species measured by both methods.

As part of this study, atmospheric C_1–C_{14} carbonyls concentrations were measured at the same sampling sites over the same sampling period (36). Average C_2–C_{10} aldehydes and monocarboxylic acids concentrations as well as average benzaldehyde and benzoic acid concentrations are listed for com-

Table 6.1: Average organic acids concentrations (μg m^{-3}) in Southern California during the photochemical smog episode of September 8–9, 1993.

Compound	San Nicolas Island	Long Beach	Central Los Angeles	Azusa	Claremont	Urban Average[a]	Ref. (14)[b]
acetic acid	1.76 ± 0.64	11.1 ± 1.5	14.7 ± 1.6	19.8 ± 2.2	16.8 ± 1.8	16.1 ± 0.9	3.42
propionic acid	0.08 ± 0.01	0.95 ± 0.05	1.55 ± 0.07	2.03 ± 0.09	1.96 ± 0.08	1.67 ± 0.04	0.31
isobutyric acid	0.02 ± 0.00	0.17 ± 0.00	0.25 ± 0.00	0.32 ± 0.01	0.35 ± 0.01	0.28 ± 0.00	0.04
butyric acid	0.01 ± 0.00	0.30 ± 0.01	0.52 ± 0.02	0.68 ± 0.02	0.75 ± 0.02	0.58 ± 0.01	0.11
pentanoic acid	0.00 ± 0.01	0.15 ± 0.02	0.28 ± 0.02	0.34 ± 0.02	0.24 ± 0.02	0.26 ± 0.01	0.06
hexanoic acid	0.02 ± 0.01	0.32 ± 0.03	0.48 ± 0.04	0.52 ± 0.04	0.27 ± 0.02	0.41 ± 0.02	0.10
heptanoic acid	0.00 ± 0.01	0.14 ± 0.02	0.18 ± 0.02	0.23 ± 0.02	0.16 ± 0.01	0.18 ± 0.01	0.04
octanoic acid	0.00 ± 0.01	0.08 ± 0.01	0.10 ± 0.01	0.12 ± 0.01	0.08 ± 0.01	0.10 ± 0.00	0.06
nonanoic acid	0.01 ± 0.01	0.09 ± 0.01	0.11 ± 0.01	0.14 ± 0.01	0.13 ± 0.01	0.12 ± 0.01	0.04
decanoic acid	0.01 ± 0.00	0.04 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	0.07 ± 0.01	0.06 ± 0.00	0.02
benzoic acid	0.01 ± 0.02	0.16 ± 0.04	0.36 ± 0.04	0.28 ± 0.04	0.38 ± 0.04	0.30 ± 0.02	0.05

[a]Average across the four urban sites Long Beach, Central Los Angeles, Azusa, and Claremont.

[b]Measurements made at a single site in 1984 at West Los Angeles; adapted from (14).

parison in Table 6.2. It is evident that the low molecular weight carboxylic acids > C_3 are present at much lower concentrations than their corresponding aldehydes while acetic acid is more abundant than acetaldehyde.

6.3.2 Diurnal Variation

Time series plots of the ambient concentrations of low molecular weight organic acids are shown in Figures 6.2 and 6.3. As a generalization, the diurnal patterns for most of the acids track each other at a given site, especially at Long Beach, indicating that they travel together as a group and probably have a common origin. The highest molecular weight alkanoic acids studied have nearly constant concentrations throughout the day and exhibit no clear diurnal behavior. The concentration profile of acetic acid is very similar to that of acetaldehyde, both in absolute magnitude and in diurnal variation (36). The diurnal variations of propionic and higher acids are also similar to those of their corresponding aldehydes, though the acid/aldehyde ratio decreases with increasing carbon number.

In the case of acetic acid and benzoic acid at Central Los Angeles, modest peaks at the time of heaviest early morning traffic (during the 6:00–10:00

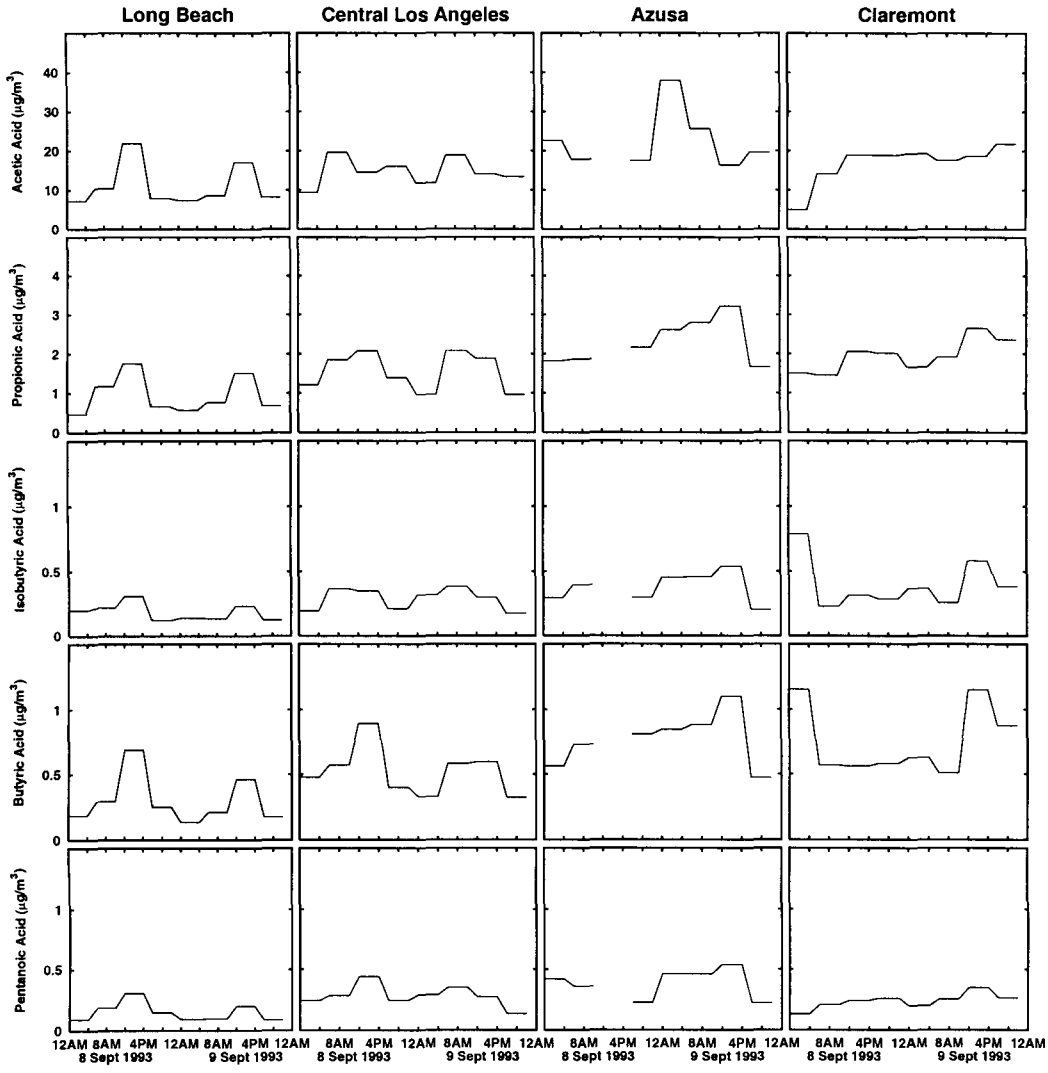

Figure 6.2: The diurnal variation of C_2–C_5 n-alkanoic acids in the Southern California atmosphere during the severe photochemical smog episode of September 8–9, 1993.

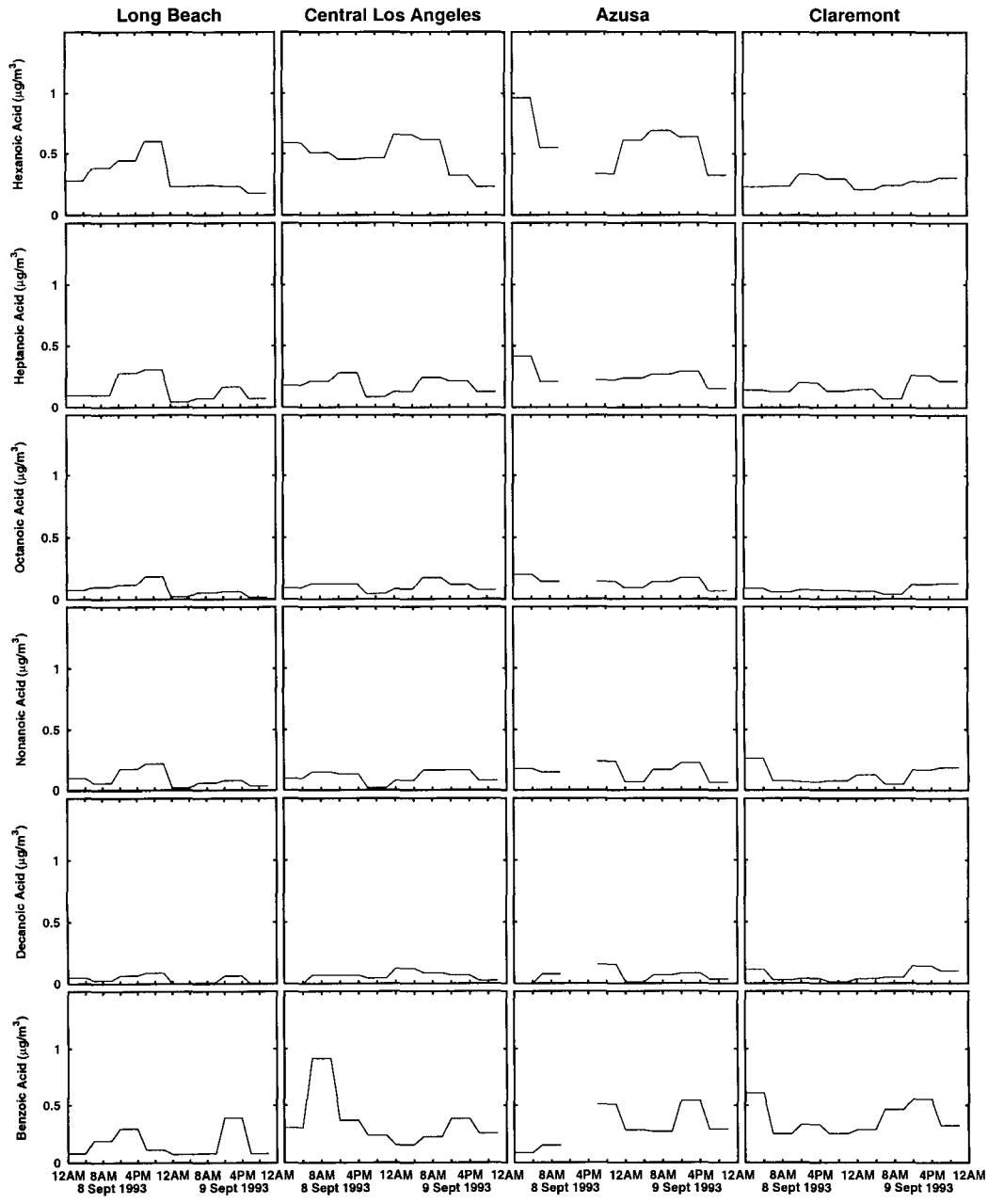

Figure 6.3: The diurnal variation of C_6–C_{10} n-alkanoic and benzoic acids in the Southern California atmosphere during the severe photochemical smog episode of September 8–9, 1993.

Table 6.2: Urban average concentrations of organic acids and aldehydes (ppbv) in Southern California during the photochemical smog episode of September 8–9, 1993.

Carbon Number	Acid	Aldehyde[a]
C_2	6.6	4.0
C_3	0.55	0.79
C_4	0.16	0.71
C_5	0.06	0.41
C_6	0.09	0.42
C_7	0.03	0.64
C_8	0.02	0.53[b]
C_9	0.02	1.09[b]
C_{10}	0.01	0.53[b]
benzoic	0.06	0.22

[a]Data adapted from Grosjean et al. (36).

[b]Measured only at Long Beach and Azusa, 6–10 a.m. and 12–4 p.m. on 9 September, 1993.

a.m. sampling period) are evident, suggesting at least some contribution from direct motor vehicle exhaust, consistent with previous studies which have found that motor vehicle exhaust is an important source of acetic acid (3). The morning rush hour peak during this experiment is much more pronounced, however, for compounds such as the hopanes and steranes, whose atmospheric concentrations are dominated by automotive exhaust (see Figure 4 in reference 37). Using the ratio of acetic acid to carbon monoxide reported by Talbot et al. in a highway tunnel (3) and scaling the carbon monoxide concentrations observed during the present field experiment by that ratio, we find that direct emissions from motor vehicles can account for no more than 13–28% of the average levels of acetic acid observed in the atmosphere. The large nighttime acetic acid peak seen at Azusa is accompanied by a similar spike in the concentrations of the industrial solvents acetone

and 2-butanone, which were measured independently and which have been reported previously (36). This suggests that acetic acid may also be emitted from industrial processes in or near Azusa.

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7 Conclusion

7.1 Summary

Methods have been developed to detect and quantify polar organic compounds in air pollution samples. A series of fine particulate source samples was silylated to look for unique polar organic compounds that could be used as tracers for those sources of fine organic aerosol in the ambient atmosphere, and those candidate molecular tracers were sought in atmospheric samples collected in California's San Joaquin Valley. In addition, gas phase formic and acetic acids concentrations at several sites in the Los Angeles air basin were analyzed to seek insights as to the origin of those compounds. Finally, a method was developed to quantify atmospheric concentrations of low molecular weight gas phase organic acids in addition to formic and acetic acids, and this method was applied to report C_2–C_{10} atmospheric organic acids concentrations during a severe photochemical smog episode.

7.1.1 Meat Smoke

Polar organic compounds in meat smoke fine particulate matter were converted to their trimethylsilyl derivatives and analyzed by gas chromatography/mass spectrometry (GC/MS). Silylation enabled the detection of monoglycerides in the meat smoke extracts and enhanced the detection of cholesterol. These compounds were detected in atmospheric fine particle samples collected in Bakersfield, California, with relative abundances that showed substantial agreement between the meat smoke source samples and the at-

mosphere. The data suggested that the saturated monoglycerides, as well as cholesterol, may be suitable for use as tracers for the atmospheric particles generated by meat cooking operations.

7.1.2 Wood Smoke

Polar organic compounds that may act as wood smoke tracers in the atmosphere were sought in wood smoke fine particulate matter by conversion to trimethylsilyl derivatives and analysis by GC/MS. Silylation enabled the detection of *n*-alkanols, plant sterols, and a number of compounds derived from wood lignin that had not previously been reported in wood smoke samples, as well as levoglucosan and related sugar anhydrides formed during the combustion of cellulose. The concentrations of these compounds measured in source emissions were compared to the concentrations in atmospheric fine particle samples collected at a rural background site and at two urban sites in California's San Joaquin Valley. On the basis of this analysis, the sugar anhydrides galactosan and mannosan were listed along with levoglucosan as being among the most abundant organic compounds detected in all samples.

7.1.3 Other Fine Particulate Emissions Sources

Vegetative detritus, motor vehicle exhaust, brake dust, tire dust, paved road dust, and cigarette smoke source samples were silylated and analyzed by GC/MS to seek polar organic compounds that may serve as tracers for those specific emission sources of atmospheric fine particulate matter. Candidate molecular tracers were also sought in atmospheric fine particle samples collected in California's San Joaquin Valley. A series of normal primary alkanols, dominated by those with even carbon number from C_{26}–C_{32}, the secondary alcohol 10-nonacosanol, and some phytosterols were prominent compounds in the vegetative detritus source sample. No new polar organic compounds

were found in the motor vehicle exhaust samples. A series of unidentified but distinctive compounds were found in the brake dust sample, and several hydrogenated resin acids were found in the tire dust sample, which might serve as useful tracers for those sources in areas that are heavily impacted by motor vehicle traffic. Finally, the alcohols and sterols emissions profiles developed for all the source samples examined in this study were scaled according the ambient fine particle mass concentrations attributed to those sources by a chemical mass balance receptor model that previously was applied to the San Joaquin Valley by Schauer and Cass (1) to compute predicted atmospheric concentrations of individual alcohols and sterols. The resulting underprediction of alkanols concentrations at the urban sites suggested that the alkanols may be a more sensitive tracer for vegetative detritus than the high molecular weight alkanes, the best previously available tracer for that source.

7.1.4 Seasonal and Spatial Characteristics of Formic and Acetic Acids Concentrations

Formic and acetic acids measurements made during the year 1986 were reported for eight sites in the Los Angeles basin and one remote offshore site. Formic and acetic acids concentrations measured in marine air upwind of the Los Angeles area over an 8-month period averaged 1.4 and 0.6 ppb, respectively, while concentrations within the Los Angeles urban area averaged 2.7–5.8 ppb formic acid and 2.9–4.2 ppb acetic acid. Average formic and acetic acids concentrations exceeded average HNO_3 and HCl concentrations, making them the most abundant gas phase acids in the Southern California atmosphere throughout the year. Formic and acetic acids concentrations near the coast changed in proportion to changes in atmospheric dilution potential, as would be expected if formic and acetic acids were emitted directly

from widespread area sources such as motor vehicle traffic. Downwind of Los Angeles, formic and acetic acids concentrations peaked during the summer photochemical smog season, and concentration changes tracked both changes in atmospheric oxidant concentrations and markers for heterogeneous conversion within clouds or fog. Formic and acetic acids concentrations thus appeared to arise both from direct emissions and from atmospheric chemical production, with the relative importance of these pathways varying spatially over the area surveyed.

7.1.5 C_2–C_{10} Organic Acids During a Severe Photochemical Smog Event

The atmospheric concentrations of gas phase C_2–C_{10} monocarboxylic and benzoic acids were determined from samples collected during a severe Los Angeles area photochemical smog episode. Average urban concentrations were 10–50 $\times$ greater than concentrations observed at a remote background location, indicating an anthropogenic origin for these compounds. Average urban concentrations during the episode were 16.1 μg m^{-3} (6.6 ppb) for acetic acid and 1.67 μg m^{-3} (0.55 ppb) for propionic acid, with progressively lesser amounts as the carbon chain length of the acids was increased. Spatial and diurnal variations in atmospheric organic acids concentrations pointed to the importance of both direct emissions from primary sources and formation by photochemical reaction of precursor compounds.

7.2 Suggestions for Further Research

There are a number of areas in which the work presented here can be expanded. The polar organic compound source emission profiles developed here can be used with the gas and particle phase emissions profiles previously de-

veloped by Schauer et al. (2–5) and Rogge et al. (6–14) in a chemical mass balance receptor model based on the use of organic compounds as tracers to hopefully improve the computed apportionment of the various sources to atmospheric fine particulate matter concentrations. Before specific polar organic compounds can be used with confidence in a source-receptor model, it will be necessary first to verify that they are conserved in the atmosphere, i.e., that they are neither formed nor destroyed by atmospheric chemical reaction, and that they are not emitted by additional sources that are unaccounted for in the model.

Another interesting extension of the work described here would be to apply these techniques to other locations, either other urban sites with different characteristics or rural areas. In such an endeavor it would be necessary to characterize fully the source emission profiles for the important sources of fine organic aerosol in those areas, using all the sampling techniques described by Schauer et al. (2). These may include other species of wood, grasses, or other biomass that is used as fuel, as well as coal combustion. In addition, it will be critical to obtain detailed ambient air quality data for the site to be modeled.

Though silylation enables the detection and quantification of a number of polar compounds that were not previously eluted from the GC column, a large fraction of the polar organic matter in atmospheric fine aerosol samples and source samples remains unidentified. Improved analytic methods to measure polymeric or other macromolecular species might aid in closing the mass balance on organic carbon. Additional derivatization techniques (15) or multiple derivatizations such as those used by Yu et al. (16) to analyze polyfunctional carbonyl compounds might be useful for this purpose.

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